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13th
EDITION

Phillips'
SCIENCE of
DENTAL MATERIALS



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Phillips' Science of Dental Materials

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13th
EDITION

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SCIENCE of
DENTAL MATERIALS

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PHILLIPS' SCIENCE OF DENTAL MATERIALS, THIRTEENTH EDITION

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Dr. Eugene W. Skinner



Dr. Ralph W. Phillips



Dr. Kenneth J. Anusavice

We would like to dedicate this edition to the first three editors of this book.

Dr. Eugene W. Skinner (I–VI), Dr. Ralph W. Phillips (V–IX), Dr. Kenneth J. Anusavice (X–XII)

Dr. Eugene Skinner, a professor of physics at Northwestern University School of Dentistry in Chicago, published the first edition of *The Science of Dental Materials* in 1936. Dr. Skinner introduced Ralph Phillips as a coauthor of the 5th edition of the book in 1960. Dr. Skinner died during the proof-page-reviewing stage of the 6th edition in 1966. He is honored with the “Eugene W. Skinner Memorial Lecture” at Northwestern University. The lecture series was renamed “Eugene W. Skinner and Eugene P. Lautenschlager Memorial Lecture” in the Department of Biomedical Engineering, Northwestern University.

Dr. Phillips renamed the book *Skinner’s Science of Dental Materials* in the 7th through 9th editions. After the death of Dr. Phillips in 1991, the book has been subsequently renamed as *Phillips’ Science of Dental Materials* since the 10th edition.

Throughout an eminent career that spanned five decades, Dr. Ralph Phillips was recognized as one of the world’s foremost leaders in the field of dental materials science. He was one of the first dental scientists to investigate the relationship between laboratory tests and clinical performance. He initiated clinical investigations designed to analyze the effect of the oral environment on restorative materials and to determine the biocompatibility of restorative materials and the efficacy of newer material formulations and techniques of use. Over his many years of service, he remained firmly committed to his original focus on the clinical relevance of laboratory findings, an approach that dominated both his style of teaching and his research activities. Among his main contributions to dentistry, Dr. Phillips pioneered studies of fluoride’s influence on the solubility and hardness of tooth enamel and its anticariogenic potential when included in restorative materials. In the 1960s, he coordinated the first workshop on adhesive dental materials, which brought together research experts in the fields of adhesion, polymer science, and tooth structure. During his career, he published more than 300 scientific papers and books and organized more than 40 symposia and conferences related to biomaterials and dental research.

Dr. Kenneth Anusavice is a Distinguished Professor Emeritus at the University of Florida and is one of the leading dental materials scientists in the field. Among his many awards, the Wilmer Souder Award for Research in Dental Materials, awarded by the International Association for Dental Research (IADR) in 1996, was one that he was most proud of. Dr. Anusavice served as the chairman of the International Organization for Standardization (ISO)/Technical Committee (TC) 106/SC 2: Prosthodontic Materials from 1999–2014 and was elected chairman of ISO/TC 106—Dentistry in 2014 until his retirement in 2016. Dr. Anusavice fostered many collaborations with different dental scientists worldwide. He was on the editorial board of numerous journals, most notably *Dental Materials* and *Journal of Dentistry*. He edited several books, contributed numerous book chapters, and published over 180 peer-reviewed manuscripts and is recognized as the foremost authority in dental materials and ceramic science. Perhaps his most significant contribution to dental materials science is his mentorship of countless students and graduate students who are now respected leaders in the research field. He received the Irwin D. Mandel Distinguished Mentoring Award, awarded by the American Association for Dental Research (AADR) in 2016, which is a true testament to his dedication to fostering the career development of students and junior faculty in the area of research in dental materials.

Front Cover

The cover image is a computer-generated fractal. Fractals are never-ending complex patterns that are self-similar along different scales, meaning that each portion can be considered a reduced-scale image of the whole. In other words, one part of the object, when magnified, will basically look like a fixed part of the whole object. This fractal phenomenon is apparent in the appearance of objects such as snowflakes and tree barks, which exist in nature. In theory, every spatial pattern that exists in this world is a fractal. See the animation of the Mandelbrot fractal¹ for self-similar characteristics.

Fractal geometry is non-Euclidean with a dimension generally expressed by a non-integer, that means with fractions instead of a whole number for Euclidean geometry: such as, 1 for line, 2 for surface and 3 for solid. For example, the fractal dimension of the west coast of Great Britain² is determined to be 1.25. The lower the dimension, the straighter and smoother the coastline is. The higher the dimension, the more tortuous and wigglier the coastline is. The ability of fractal geometry to describe simply otherwise complex lines and surfaces has led to its application in many fields

of chemistry, physics, engineering, computer science and materials science.

One noted example of using fractal analysis in dental materials science is the analysis of fracture surfaces of restorations. When a material fractures in a brittle manner, the fracture surface records the event in such a way that many important features associated with the stresses which caused the fracture are made clear. Rather than stating that a surface is either rough or smooth, the fractal dimension of the surface provides the means to assign a numerical “grade” to the tortuosity. Experimental observations³ demonstrate that the fracture toughness of ceramic materials is proportional to the square root of their fractal dimension increment (D^*). D^* is equal to the non-integer portion of the fractal dimension and lies somewhere between 0 and 1.

Fractal analysis can be a powerful forensic tool for clinical evaluation of ceramic restorations⁴. In many cases for which the failure site has been retrieved, the researcher can distinguish between failures caused by overload and processing errors as each mode of failure should have distinct fractal dimensions of the materials used.

¹Mandelbrot fractal set: https://en.wikipedia.org/wiki/Mandelbrot_set.

²Mandelbrot BB: How long is the coast of Britain? - Statistical self-similarity and fractional dimension. *Science* 156:636-638, 1967.

³Griggs JA: Using fractal geometry to examine failed implants and prostheses. *Dent Mater* 34:1748-1755, 2018.

⁴Mecholsky JJ, Hsu SM, Jadaan O, Griggs J, et al: Forensic and Reliability Analyses of Fixed Dental Prostheses. *J Biomed Mat Res* 01 Feb 2021, <https://onlinelibrary.wiley.com/doi/10.1002/jbm.b.34796>.

Preface

The dentist and the engineer have much in common. Dentists design restorations and prostheses that must endure in the oral cavity. In the process, dentists make informed decisions from personal experience and existing clinical evidence to conceptualize the optimal design of the prosthetic structure and final restoration. Like engineers, dentists must be aware of the design principles and possess sufficient knowledge of the physical properties of the various types of materials they use. The goal is to exercise the best evidence-based judgment possible in their selection of design and materials. For example, dental professionals must know whether the clinical situation, such as a large restoration, requires the use of an amalgam, a resin-based composite, a cement, a casting alloy, a ceramic, or a metal-ceramic. In addition to the mechanical requirements of the materials that are within the training experience of an engineer, the esthetic and physiological requirements are essential for the dentist.

The aims of this textbook are to (1) introduce the basic materials science relevant to dental applications to readers with little or no prior engineering background, (2) describe the basic properties of dental materials that are related to clinical manipulation by either dentists and/or dental laboratory technicians, (3) characterize the durability and esthetics of dental restorations and prostheses made from biomedical materials, and (4) identify characteristics of materials that affect tissue compatibility and general biological safety. The technology and information provided are intended to bridge the gap between the knowledge of biomaterials obtained in basic courses in materials engineering, chemistry, and physics and the use of the materials in the dental lab and dental clinic. The emphasis of the book remains on the *why* rather than the *how* in the selection and use of dental materials and how the oral environment affects materials. The manipulation parameters required for maximum performance are stressed throughout. Nonetheless, the reader is encouraged to understand the rationale for the selection of a particular material or technical procedure.

The chronology of the presentation of the subjects in this edition follows the format of the 12th edition, with some modifications. For the 13th edition, one new section and three new chapters are added, together with the merging of some chapters into one. This edition has 20 chapters divided into five four-chapter sections to reflect the focus of the chapters in each section. Part I, General Classes and Properties of Dental Materials, covers the fundamental information for the scope of dental materials and their physical/mechanical properties relevant to the selection of materials for dental applications. [Chapter 1](#) was revised to focus on the role of materials in clinical dentistry. The topics of metals and polymers are merged with [Chapter 2](#), along with a brief introduction to ceramics and composites. Part II, Direct Restorative Materials, is focused on four groups of materials: resin-based composites, bonding and bonding agents, dental cements, and dental amalgams. Part III, Indirect Restorative Materials, is focused on the use of metals, den-

tal ceramics, denture base resins, and dental implants. The major change is merging dental casting alloy, metal joining, and wrought metals into one chapter. Part IV, Fabrication of Prostheses, covers the materials needed and the technology of making metallic prostheses from basic ingredients. Chapters on impression materials, gypsum products, and dental waxes are merged as [Chapter 13](#), Auxiliary Materials. A new chapter entitled Digital Technology in Dentistry ([Chapter 15](#)) was added. Part V, Assessing Dental Restorations, is a new section comprising two existing chapters ([Chapters 17 and 20](#)) and two new chapters ([Chapters 18 and 19](#)). The rationale of this section and the chapters included are discussed in the “Organization of the Book” section of [Chapter 1](#).

Several of the chapters represent significant changes in approaches to the specific subject. [Chapter 1](#), Overview of Dental Materials, has been revised to include a brief description of tooth structure and the potential issues occurring that require intervention. Examples of issues and recognized treatments are discussed. The topics of the evolution of biomaterials and the standards for safety and quality assurance are distributed among [Chapters 17, 18, and 20](#). After merging with the materials on metals and polymers, [Chapter 2](#), Structure of Matter, General Classes of Materials, and Principles of Adhesion, is organized in the following sequence: structure of atoms and molecules, bonds between atoms and between molecules, crystalline versus amorphous structure, the resultant classes of materials (metals, ceramics, and polymers) from bonding, general properties of each class of material, the key components of the fourth class of material, composites, and principles of adhesion. Keep in mind that the composites discussed here are not limited to those used in dentistry. The chapter delineates the role of adhesion (bonding) in the formation of materials. The significance of bonding is reinforced in [Chapters 5, 6, 7, 8, 9, and 10](#). Finally, [Chapter 20](#), Emerging Technologies, describes recently emerged technologies with the potential for dental applications and projects potential future technologies in dentistry.

Three new chapters are added in this edition. Over the last two decades, new digital technologies and digital equipment have been introduced to the dental community and matured. [Chapter 15](#), Digital Technology in Dentistry, presents an overview of dental imaging and computer-aided design/computer-aided manufacturing (CAD-CAM) technologies, such as digital impressions, milling, and three-dimensional (3-D) printing, and the materials currently used for each process. The use of digital technology for making prostheses, CAD-CAM, is also addressed in [Chapters 9](#) (Metals), [10](#) (Ceramic-Based Materials) and [11](#) (Prosthetic Polymers and Resins).

Dental materials research has become specialized in techniques and data analyses, and the clinical relevance of in vitro research is often questioned. [Chapter 18](#), In Vitro Research on Dental Materials, discusses the importance of in vitro research in developing

improved preventative, restorative, and auxiliary materials and the limitations of in vitro research when making clinical decisions. Computer modeling methods and statistical methods for forecasting clinical performance based on data gathered in vitro are also discussed.

The ultimate test for a restorative material is clinical performance as a restoration, including longevity and predictability of use. [Chapter 19](#), Clinical Research on Restorations, discusses clinical performance testing of dental biomaterials, which is considered the most valid test of a material's behavior in the oral environment. The various types of clinical studies are discussed, along with the advantages and disadvantages of each. Also, this chapter describes existing analytical methods for assessing performance.

As with the last two editions, each chapter contains a section of key terms with definitions that are designed to familiarize the reader with the content of the chapter and a number of critical thinking questions that are intended to stimulate thinking and emphasize important concepts. The answers to these questions are generally found in the section or sections immediately following each question. The selected key terms listed are associated with the content of the chapter, but the list is not intended to be a glossary of the chapter. In this edition, the 10 most relevant references are cited in the book, and the remaining references are stored online.

Chiayi Shen

H. Ralph Rawls

Josephine F. Esquivel-Upshaw

Acknowledgments

In a revision of this magnitude, the editors must draw upon the expertise of colleagues and friends. Equally important, if not more, is a book with a solid foundation that will facilitate the process. We are blessed that Dr. Eugene W. Skinner, Dr. Ralph W. Phillips, and Dr. Kenneth J. Anusavice built the foundation of the book over three-quarters of a century. Many individuals should be recognized both for their contributions to the field of dental materials science, to earlier editions, and to the revision of this textbook.

Novel suggestions were made on the reorganization and the content of the 13th edition to adapt to the ever-changing needs of the dental community. Dr. Saulo Geraldelli made significant contributions to [Chapter 1](#) to provide an overview of preventive and restorative materials. Dr. William Brantley made significant contributions to [Chapter 2](#) on classes of materials and adhesion, and merged all metal subjects, except amalgam, in [Chapter 9](#). Dr. Kyumin Whang wrote [Chapter 5](#) and contributed to revision of [Chapter 6](#) on bonding agents and [Chapter 20](#) on emerging technologies. Dr. Carolyn Primus revised [Chapter 7](#) on cements and made major contributions to the revision of [Chapter 20](#). Drs. Rodney Phoenix and Larry Gettleman, both renowned prosthodontists, coauthored [Chapter 11](#) on prosthetic polymers and resins. Dr. Gettleman also assisted in [Chapters 14](#) and [20](#). The revision of [Chapter 12](#) on dental implants was coauthored by Dr. Jack Lemons, an internationally recognized expert on implant materials and designs. [Chapter 15](#) is a new chapter on digital technology by Dr. Ralph Rawls and Dr. Jacob Park. Dr. Charles DeFreest made significant contributions to the revision of [Chapter 16](#) on finishing and polishing. Dr. Gottfried Schmalz revised [Chapter 17](#) on biocompatibility. Dr. Jason Griggs contributed to [Chapter 18](#) on in vitro testing on dental materials; this is new to the 13th edition and should prove valuable in elucidating laboratory tests for materials prior to marketing. [Chapter 19](#) on clinical research on

restorations is a new chapter by Dr. Josephine Esquivel-Upshaw. [Chapters 18](#) and [19](#) discuss the strengths and weaknesses of both categories of research and stress the need of keeping a balance.

Much of the artwork came from the 12th edition and was created by Jeannie Robertson. Other artwork that was reprinted from the 11th edition was created by Dr. José dos Santos, Jr.

We express our appreciation to those who contributed to the 12th and earlier editions of this textbook but who were not contributors to the 13th edition. Several of the revised chapters contain portions of sections from contributors to previous editions. These contributors include Drs. Grayson Marshall Jr., Sally Marshall, Barry Norling, Sibel Antonson, Erica Texeira, Qian Wang, John Wataha, Jack Ferracane, Rodway Mackert Jr., Karl-Johan Söderholm, Harold Stanley, and Mr. Paul Cascone. These individuals provided significant input to the 12th and/or earlier editions, in which several significant changes had been introduced to enhance readability and the clinical perspectives on dental biomaterials. In their quest to promote evidence-based dentistry, they blended basic science, clinical science, and applied or translational research findings with processing and manipulation variables to optimize production and clinical outcomes.

We would also like to acknowledge the immense contribution of Dr. Kenneth Anusavice to the 10th through 12th editions of this book. He is a true inspiration for all dental materials scientists because he bridged the gap between laboratory and clinical applications. We also thank his wife, Dr. Sandi Anusavice, for assisting with grammatical edits for this edition.

Finally, we would like to thank the staff at Elsevier Inc. for their assistance in organizing and expediting the activities related to publishing the 13th edition. These individuals include Alexandra Mortimer, Joslyn Dumas, and Kathleen Nahm during the planning and writing phase, and Umarani Natarajan and Radhika Sivalingam in the editing and production phase.

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Phillips' Science of Dental Materials

1

Overview of Dental Materials

OUTLINE

The Oral Cavity

Structure of Teeth

Potential Issues and Treatments Associated With Teeth

Categories of Dental Materials

Challenges of Dental Materials in the Oral Cavity

The Future Need for Dental Biomaterials

Organization of the Book

KEY TERMS

Auxiliary dental material Substance used in the construction of a dental prosthesis that does not become a part of the prosthesis.

Preventive dental material Cement, coating, or restorative material that either seals pits and fissures or releases a therapeutic agent, such as fluoride and/or mineralizing ions, to prevent or arrest the demineralization of the tooth structure.

Restorative dental material Metallic, ceramic, metal-ceramic, or resin-based substance used to replace, repair, or rebuild teeth

and/or enhance esthetics. A direct restorative material is placed in the tooth preparation and is transformed to be a restoration. An indirect restorative material is fabricated extraorally to produce prostheses.

Temporary restorative material Cement or resin-based composite used for a period ranging from a few days to several months to temporarily restore or replace missing teeth or tooth structure until a definitive, lasting prosthesis or restoration can be placed.

Dentists and engineers have similar long-range objectives in their professions—that is, to design, construct, apply, and evaluate devices or structures of materials that can be subjected to a wide range of environmental conditions. They must have a thorough knowledge of the properties and behavioral characteristics of the materials they intend to use. However, dentists need to make proper diagnoses, prevent dental caries, and surgically treat the affected tooth structures. Subsequently, they must select a material, or materials, for either direct or indirect applications aiming to restore the patient's intraoral functions. The science of dental materials covers a broad range of terminology, composition, microstructure, and properties used to describe or predict the performance of materials developed for dental applications. Previous courses in mathematics, chemistry, and physics should have prepared you to read this book and understand the terms and principles involved in describing the behavior of these materials as they are used clinically and in the testing laboratories of academia, governmental facilities, and industry.

Properties of materials can be categorized into chemical and physical properties. Chemical properties are generally composed of the composition and behavior of materials in a chemical environment, regardless of any interaction with other external influences. These properties will be presented in chapters where specific materials are discussed. Physical properties ([Chapter 3, Introduction](#)) are measurable variables that describe how an object looks, feels, or acts when the object is probed by external agents, such as heat, light, moisture, or force. Mechanical properties are an aspect of physical properties, primarily related to the behavior of materials in response

to externally applied forces or pressures ([Chapter 4, What Are Mechanical Properties?](#)). In a clinical environment, the behavior of dental materials may depend on several variables simultaneously, but our ability to differentiate primary from secondary factors or properties will allow us to easily understand or predict a material's performance. Furthermore, this potential to predict clinical performance will allow us to analyze the causes of structural degradation and failure of these materials when they no longer serve their intended functions in the oral cavity.

In this chapter, we will describe the function of the oral cavity, the structure of the tooth, potential issues involving teeth that require intervention, categories of materials by application, challenges to these materials in restoring the function of the teeth, safety issues of dental materials, the future need for dental biomaterials, and the organization of the book.

The Oral Cavity

As an anatomical space and part of the head and neck, the oral cavity consists of the lips, cheeks, minor salivary glands, gingiva, tongue, hard palate, and teeth. As part of human evolution, the oral cavity developed to allow humans to ingest food, chew, swallow, breathe, and speak.

In addition, the oral cavity is a food processor for the body. The presence and colonization of bacteria, along with distinct teeth anatomy, saliva, and chewing (motion), begin the breakdown of food and initiate the digestive process. Therefore humans are able

to obtain the nutrients necessary for survival. Furthermore, both biting and chewing require upper and lower jaws, muscles, and teeth working in unity to achieve this goal. A distinctive component required in this interaction (Figure 1-1, A) to cut and grind food is force. You will find throughout this book that the term *force* is often used, so a proper presentation of the term is warranted.

CRITICAL QUESTION

How is force generated, and how do we measure the quantity of force?

What Is Force?

In classical physics, *force* is defined as the interaction between two objects during the action of push or pull. When opposing teeth come into contact during occlusion, an interaction occurs, and *forces* act upon the teeth in contact. Thus one can say that force exists as the result of an interaction, or when two objects contact one another. According to Newton's third law of motion, for every action, there is an equal and opposite reaction, or in other words, for every interaction, there is a pair of forces going in opposite directions coming from both objects (Figure 1-1, B). When this interaction ceases, or when teeth do not occlude, the two objects no longer experience force. However, not all interaction requires physical contact. For example, objects fall to the ground because the earth's gravity constantly pulls objects toward the earth.

Force is a vector that has direction and magnitude. The quantity of force is measured using a unit known as *Newton*, abbreviated with an "N." One Newton is the amount of force required to give a 1-kg mass an acceleration of 1 m/s^2 , which means that $1 \text{ N} = 1 \text{ kg} \cdot \text{m/s}^2$. Acceleration makes a stationary object come into movement. We know that the Earth's gravitational acceleration is about 9.8 m/s^2 . Therefore gravity exerts a force of 9.8 N on an object with a mass of 1 kg. If this object is resting on a tabletop, a force of 9.8 N will be exerted on the area of contact. Furthermore, if we assume this area of contact is 100 mm^2 ($= 1 \times 10^{-4} \text{ m}^2$), and we divide the applied force by the area, we obtain a value of 0.098 N/mm^2 ($= 9.8 \times 10^4 \text{ N/m}^2$) for the force, known as *pressure*, on the surface. The International System (SI) unit of pressure is N/m^2 , which is also called *Pascal* (Pa). The force applied by the weight of the object is distributed throughout the supporting substrate as internal stress and can cause a strain, or deformation of the substrate. Stress is calculated by dividing the force by the cross-sectional area of the substrate and has the same

SI unit as pressure. The concept of stress and strain will be discussed in Chapter 4, *Stress and Strain*.

Mastication and Clenching Forces

The range of biting forces varies markedly from one area of the mouth to another and from one individual to another. The most quoted maximum bite forces range from 400 to 890 N for molar teeth, 222 to 445 N for premolars, 133 to 334 N for canines, and 89 to 111 N for incisors. Although there is considerable overlap, biting force generally is greater for males compared with females and for young adults compared with children.

A 2002 study reported a mean clenching force of 462 N, with a range of 98 to 1031 N for individuals between the ages of 28 and 76 (mean age = 46) who had lost their posterior teeth. In comparison, subjects with a complete dentition exerted a mean clenching force of 720 N with a range of 244 to 1243 N. If a force of 756 N is applied to a cusp tip over an area equivalent to 3.9 mm^2 , the compressive stress would be 193 MPa ($1 \text{ MPa} = 1 \times 10^6 \text{ Pa}$). If the area is smaller, then the stress within the cusp would be proportionately greater. The *Guinness Book of Records* (1994) lists the highest human bite force as 4337 N sustained for 2 s. The average maximum sustainable bite force is approximately 756 N.

Taking this information into consideration, one may ask what attributes or characteristics allow the tooth to sustain such force. Let us pause and familiarize ourselves with the structures of the tooth.

CRITICAL QUESTION

How does the structure of the tooth enable resistance to fracture from occlusal loading?

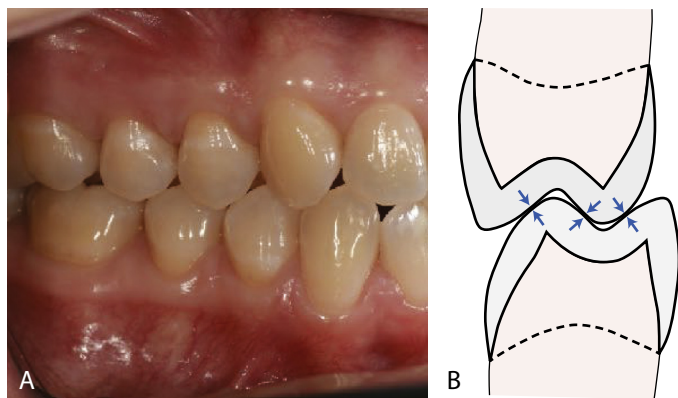
Structure of Teeth

In the oral cavity, teeth are firmly joined to the upper and lower jaws by tooth-supporting connective tissues (cementum, periodontal ligament). This assembly of tissues ensures enough flexibility to withstand the forces of mastication and act as thermal and chemical insulators. Teeth perform important functions in the oral cavity. The front teeth can grab and cut food to a size that is suitable for the mouth (bite-size). They also have a role in speech and contribute to facial aesthetics. The posterior teeth's morphology is designed to grind the bite-size food into smaller sizes, which facilitates food passage from the throat to the stomach.

At the teeth's full formation and physiological capacity, they will have the following structures: enamel, dentin, enamel-dentin junction, pulp, and cementum (Figure 1-2).

Enamel

Dental *enamel* is a biologically ceramic composite made of precisely arranged 20-nm-diameter fibrous apatite crystals (92 to 94 vol%). The meaning of *composite* will be discussed in Chapter 2, *Composite Materials*. The remaining nonmineral content (2 to 4 wt%) is represented by water, lipids, and several peptides. This small amount of nonmineral components, along with its hierarchical anisotropic structure, regulates the mechanical properties of enamel to respond to the tooth's functional needs, such as strength and resistance to wear upon loading. On a micrometer scale, enamel contains rod and interrod structures (Figure 1-3), beginning at the enamel-dentin junction and extending to the tooth surface. The



• **Figure 1-1** Interaction between teeth. **A**, Natural human dentition of an adult patient showing upper and lower teeth in full-occlusion contact. **B**, Forces acting on teeth at occlusion.

ability of the rigid rod structure, along with the organic interrod component, to weaken the stress concentration at the crack tip, if present, improves the resistance of the enamel to fracture from the stress generated at the surface contact.

Dentin

Dentin is a composite mineralized tissue that contains less mineral than enamel and is composed of nanocrystalline carbonated hydroxyapatite (Figure 1-4). The organic content (30 vol%) is almost exclusively type I collagen fibrils plus noncollagen proteins, such as proteoglycans. In addition, this tissue has a peculiar morphological feature: the presence of tubules extending from the enamel-dentin junction to the pulp. These tubules have

diameters varying from 2.5 μm near the pulp tissue to 0.8 μm at the enamel-dentin junction. They also run transverse to the root or in an S-shape in the crown. This anisotropic, hierarchically oriented, and less mineralized microstructure serves as a foundation, shapes the roots, and protects the pulp. When loaded intraorally and force is applied parallel to the tubules, dentin responds better mechanically than when loads are applied perpendicularly.

Dentin-Enamel Junction

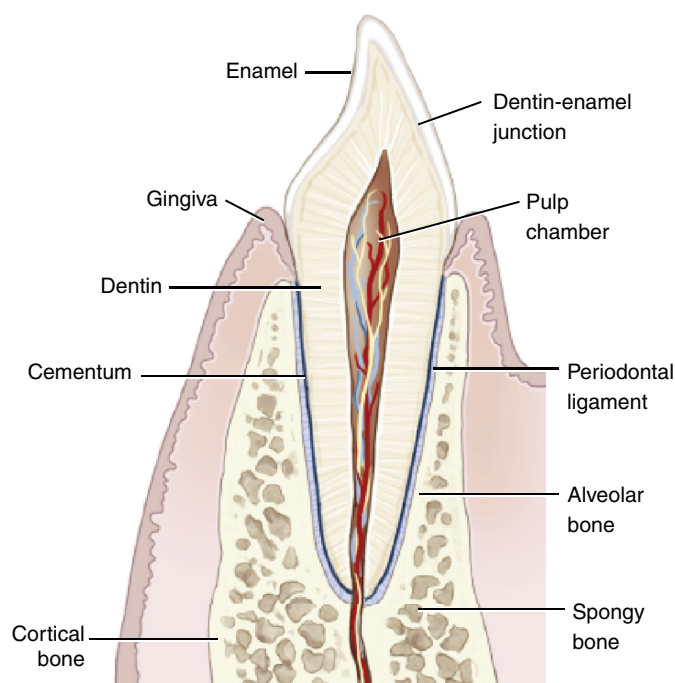
Between the harder, brittle enamel and the softer, durable (tough) dentin, a functionally graded junction, the dentin-enamel junction (DEJ), is present, allowing a smooth transition of loads from the enamel to the dentin (Figure 1-5). This interface inhibits the propagation of cracks from the enamel to the dentin, thus supporting the tooth's integrity during masticatory actions. Even though fracture lines between enamel and dentin appear as a result of continuous masticatory action and/or occasional impact loading, enamel infrequently debonds from dentin, making the DEJ highly resistant to damage.

Cementum

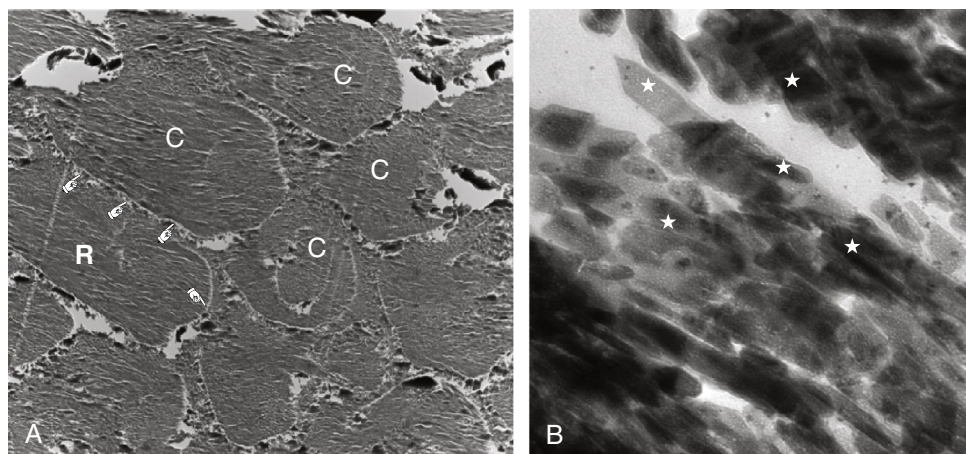
Cementum is a mineralized tissue covering the entire root surface of the tooth. Cementum is composed of water, organic matrix, and mineral. About 50% of the dry mass is inorganic and consists of hydroxyapatite crystals. The remaining organic matrix is largely made up of collagen and, to a lesser degree, glycoproteins and proteoglycans. The main function of cementum is to support or anchor the tooth, together with the principal periodontal fibers and alveolar bone.

Pulp

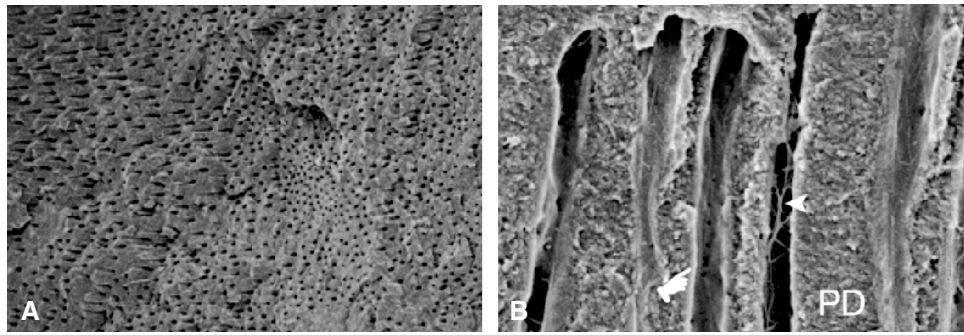
The dental pulp is centrally located in the pulp cavity and quite often resembles the external surface of the tooth. This specialized, loose, fibrous connective tissue is composed of collagen fibrils and organic ground substance composed of 75% water and 25% organic material. As an organ, the pulp fulfills key physiological functions, namely, formative or developmental (generates dentin), nutritive (supplies nutrients and moisture through the vascular system), protective (responds to injury and noxious stimuli), and



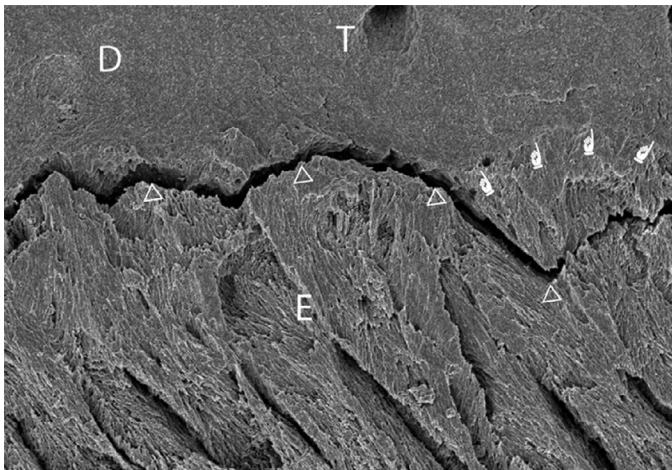
• **Figure 1-2** Schematic cross-sectional view of a natural anterior tooth and supporting tissues.



• **Figure 1-3** Transmission electron microscope images of sound enamel. **A**, High-resolution image of enamel depicting the structural organization between rods (R) and interrods (C) ($\times 3\text{K}$). **B**, Ultrahigh-resolution image showing the distribution of crystal in one rod (white star). The semiwhite spaces between crystals are porosities ($\times 200\text{K}$).



• **Figure 1-4** Scanning electron microscopy images of fractured sound dentin specimens. **A**, Massive presence of open tubules ($\times 400$). **B**, Higher magnification of a longitudinal fracture allowing the visualization of intertubular dentin (PD), peritubular dentin (*white index*), and the organic structure lying free within the dentinal tubule known as *lamina limitans* (*white arrow*) ($\times 4000$).



• **Figure 1-5** Scanning electron microscopy image of the dentin-enamel junction region of sound human tooth showing dentin (D), enamel (E), and dentinal tubule (T). The pointers depict the smooth transition between the enamel and dentin. Because of the structural difference between the enamel and the dentin, cohesive separation at the interphase, indicated by Δ , is an artifact from sample preparation.

sensory (nerve fiber network transmits afferent pain). Whenever possible, especially while using dental materials, preserving the health of such vital tissue is highly desired.

Potential Issues and Treatments Associated With Teeth

Taking into consideration the lifespan and lifestyle of humans, there are three categories of issues that may affect and change the normal appearance, structure, position, and function of teeth to undesirable outcomes that require intervention to restore their function. These categories are biological, genetic, and mechanical in nature.

Biological Issue

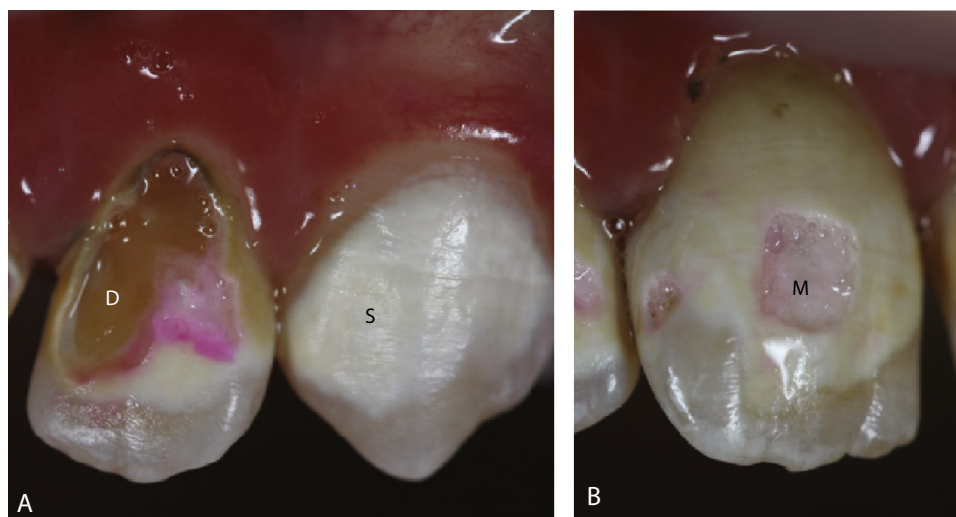
The oral cavity is an open ecosystem with the most diverse microbial communities in the body and is constantly under threat. The oral cavity is also where digestion of food begins (solid and liquid) and the apparatus that humans use to communicate. In this environment, the inevitable interaction between bacteria, saliva, oral hygiene, and diet can lead to health or disease. If such interaction favors a balance

among these factors, then oral health is promoted. On the other hand, if an imbalance takes place (i.e., poor oral hygiene and high-sugar diet), carious lesions will develop, leading to superficial (S), moderate (M), and deep (D) active lesions ([Figure 1-6](#)).

Superficial active carious lesions are usually located at the enamel level only and appear chalky ([Figure 1-6, A](#)). If these lesions are located on smooth buccal or lingual surfaces, they are known as *white spot lesions* (WSLs). WSLs can be treated by application of either highly fluoridated materials or through the infiltration of polymerizable, unfilled, low-viscosity adhesive resins. If the superficial lesions are present in grooves, pit and fissure sealants are used. Clinically, placing sealants in noncarious grooves is recommended for pediatric and adolescent patients at high caries risk. All treatments discussed do not involve surgical intervention but utilize, in part, the porosity of tooth structure caused by the carious process for infiltration of fluoride ions or fluid polymerizable monomers for protection against further acid attack. Moderate to deep carious lesions indicate loss of tooth structures, quite often with exposed dentin substrate ([Figure 1-6, A & B](#)). Unfortunately, these clinical occurrences require the use of sharp burs and/or hand instruments to remove the affected tissues and reshape the remaining tooth structures to accommodate the restorative dental biomaterial selected. The materials can be composites, ceramics, or metals, as will be discussed later. A myriad of preparation designs (reshaping), such as cavity preparation, inlays, onlays, and full crowns, are available. In cases of extensive carious lesions that affect several teeth, partial or even full-mouth teeth extraction is the only solution. To recover the patient's ability to chew and speak in the case of tooth loss from extraction or trauma, prosthetic appliances such as dental bridges, implants, and complete dentures are used.

Genetic Issue

Across the world, in all countries and cultures, observing people with misaligned or deficient bites when they smile or speak is not uncommon. Such phenomena, termed *malocclusion*, can be caused by extra teeth, lost teeth, impacted teeth, or abnormally shaped teeth. A small underdeveloped jaw, caused by a lack of masticatory stress during childhood, can cause tooth overcrowding ([Figure 1-7, A](#)). Crowding of the teeth can be treated with orthodontics, often through planned tooth extractions, clear aligners, and/or dental braces. Braces are sets of flexible metal wires and brackets made of metal or ceramic materials. Brackets are cemented to the teeth ([Figure 1-7, B](#)), and wires are tightened



• **Figure 1-6** Active carious lesions in anterior teeth. **A**, Chalky appearance of demineralized enamel represents superficial (S) carious lesion, and dark-brown exposed dentin shows deep (D) carious lesion. **B**, Medium (M) carious lesion represented by the loss of enamel before exposing dentin.



• **Figure 1-7** Genetic issue. **A**, Misaligned lower anterior teeth. **B**, Ceramic/metal-base orthodontic braces were bonded to the enamel to move teeth to proper position. **C**, A metal wire is attached to the lingual enamel of the lower anterior teeth to prevent drifting of the teeth, which would compromise the planned clinical outcome. (Courtesy Dr. Adalberto Paula Souza, Jr.)

and adjusted over time so that the elastic properties of the wire gradually apply enough force to move the teeth into the desired alignment. However, teeth naturally tend to drift out of place, even after treatment with braces. As a result, wearing a retainer made of wires and acrylic resin or wires bonded to the tooth (**Figure 1-7, C**) may be needed to keep newly aligned teeth from moving.

Mechanical issue

The interaction between opposing teeth that enables the size reduction of food also leads to the wearing down of teeth, which is known as *attrition* and is often associated with masticatory force and parafunctional activity. Attrition mostly causes wear of the incisal and occlusal surfaces of the teeth. Although a certain degree of attrition is normal, unnecessary loss of tooth structure at the cementum-enamel junction can also occur in the presence of unbalanced stresses, friction, biocorrosion (chemical, biochemical, and electrochemical degradation), or a combination of these. Studies have reported that the prevalence of attrition in the population can reach as high as 75%. Clinical examples are *bruxism/clenching*, caused by repetitive jaw-muscle parafunction activity leading to occlusal excessive wear; *abfraction* (static stress

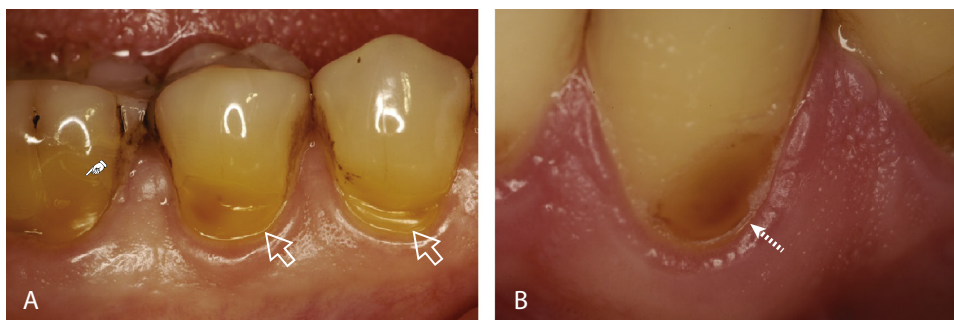
biocorrosion); and *abrasion/biocorrosion*, caused by the action of acidic food and/or beverages, as well as toothbrushes, on the surface of the teeth (**Figure 1-8**). Treatment options that require the use of dental materials include fabrication of an occlusal guard to deprogram masticatory muscles and avoid grinding and clenching, restorations to prevent further wear and decrease sensitivity, and “full-mouth rehabilitation” for severe cases. In cases of tooth fracture, the extension and remaining amount of the tooth structures dictate the approach (i.e., restoration or extraction) and the selection of the restorative dental biomaterial.

CRITICAL QUESTION

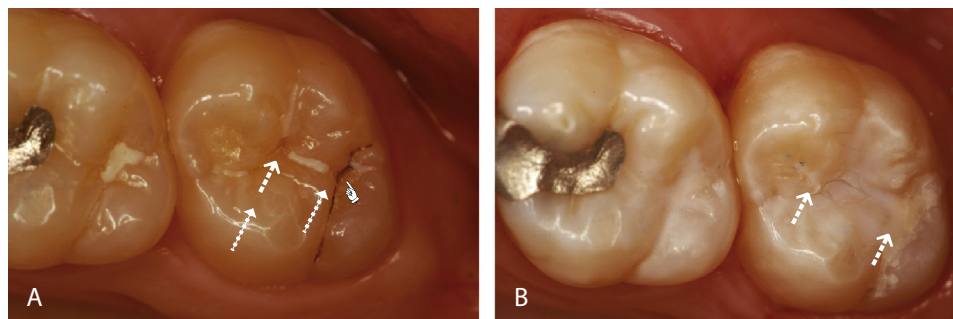
What are the differences among preventive, restorative, and auxiliary dental materials used when constructing a fixed dental prosthesis (FDP)?

Categories of Dental Materials

Dental materials may be fabricated using any of the four classes of materials: metals, ceramics, polymers, or composites discussed in **Chapter 2**. From the viewpoint of intended applications, they are classified as preventive, restorative, and auxiliary.



• **Figure 1-8** Noncarious cervical carious lesions. **A**, Erosion (*triangle*). **B**, Biocorrosion (*pointers*).



• **Figure 1-9** Preventive sealant. **A**, One sealant (*dashed white arrow*) that needs repair and an area of a deep groove planned to receive sealant (*pointer*). **B**, Sealant repaired and a new one placed.

Preventive Materials

Preventive dental materials usually include polymer-based materials that seal susceptible surfaces of the tooth (i.e., pits and fissures) against caries (Figure 1-9) and/or release fluoride or other therapeutic agents to prevent or inhibit the progression of tooth decay (dental caries). The service life of restorative materials may be limited to a short-term application (up to several months) or moderately long time periods (1 to 4 years) when they are used to release therapeutic agents. This is because either the materials deteriorate as they release the therapeutic agents, or they lose their preventive capability as the release rates fall below the therapeutic limit.

Restorative Materials

After successful treatment of the disease and removal of the infected tissue, the obvious loss of the tooth structure needs restoration. Depending on the amount of tooth-structure loss, the restoration can be a filling, inlay/onlay, full crown, bridge, implant, or denture.

Restorative dental materials consist of synthetic components that are used to repair or replace tooth structure. They are grouped by composition, specific function, the type of tooth structure they are replacing, or method of fabrication. This section will focus on the method of fabrication, which is classified into direct and indirect restorative materials. However, a temporary restoration is often needed before the final definitive restorations are delivered, especially for indirect restorations.

Direct Restorative Materials

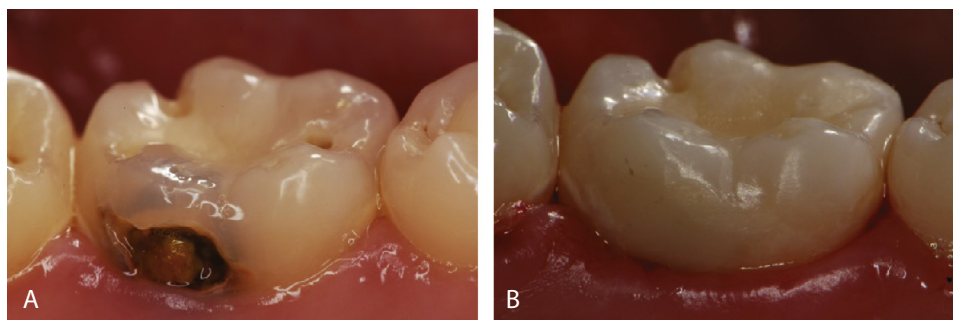
Direct restorative materials are a group of materials placed directly into a designed tooth preparation that go through a phase transformation from a flowable or moldable state to a functional, solid state while they are being adapted to the preparation. Pure gold

in foil form, for example, can be used to make dental restorations (“fillings”) directly on the teeth, but this technique is rarely used today. Amalgam alloy is a metallic powder containing silver, tin, and copper, which generates a condensable (moldable) mixture that allows placement and carving at the intraoral temperature within a reasonable working time when mixed with mercury. Once this mixture hardens, the solid exhibits enough strength to perform duties as a tooth-replacement material (Chapter 8, Introduction).

In a similar way, glass or ceramic particles of different sizes (micron to nano), shapes, and compositions are incorporated into a variety of liquid monomers to generate the so-called resin-based composite materials. As a result, composite materials of different viscosities and compositions are formulated. Clinically, this group of materials can be transformed from moldable to a solid state within a short period of time when two components are mixed or when a single component, as received, is exposed to a high-intensity blue light (Figure 1-10). The mechanism of transformation of the former is called *chemical polymerization*, and the latter is called *photopolymerization*, giving dental practitioners timeless control when manipulating, inserting, or sculpting the material intraorally (Chapter 5, History of Composites). One unique aspect that characterizes these materials is their capacity to micromechanically adhere to the teeth and other dental material substrates via bonding mechanisms. This aspect fostered the concept of minimally invasive dentistry. Their capacity to mimic or reproduce tooth color is highly relevant.

Indirect Restorative Materials

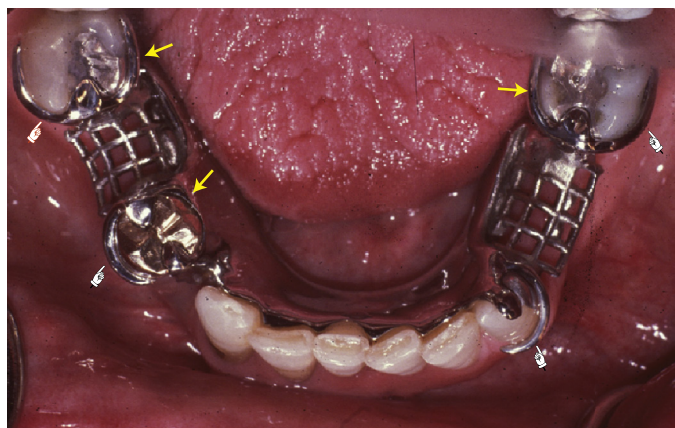
During their assembly, some restorations and prostheses undergo intra- and extraoral steps before placement in the oral cavity (Figure 1-11, A & B). These materials and techniques are meant to replace large areas of lost tooth structure, in addition to actual



• **Figure 1-10** Direct composite restoration. **A**, An active/arrested carious lesion at the lingual surface on a lower molar tooth. **B**, After surgical removal of the infected carious tissues, a direct restorative material was placed.



• **Figure 1-11** Indirect ceramic restoration. **A**, Tooth preparation isolated with rubber dam. **B**, Indirect ceramic restoration made and adapted to a stone cast. **C**, Clinical view of the tooth/ceramic assembly after finishing the adhesive luting steps. (Courtesy Dr. Karine Barizon.)



• **Figure 1-12** A removable partial denture framework in place. The pointers indicate the retentive arms, and the arrows indicate the reciprocal arms. The wire mesh area between teeth provide sites for retaining artificial teeth with tissue-colored denture resin.

teeth. They are generally called *indirect restorative materials* and can be fixed by cementation (Figure 1-11, C) or remain removable, like a partial denture held by friction (Figure 1-12), or a complete denture (Figure 1-13), which is held to soft tissue by wetting. The issue of wetting will be discussed in Chapter 2, *Wetting*.

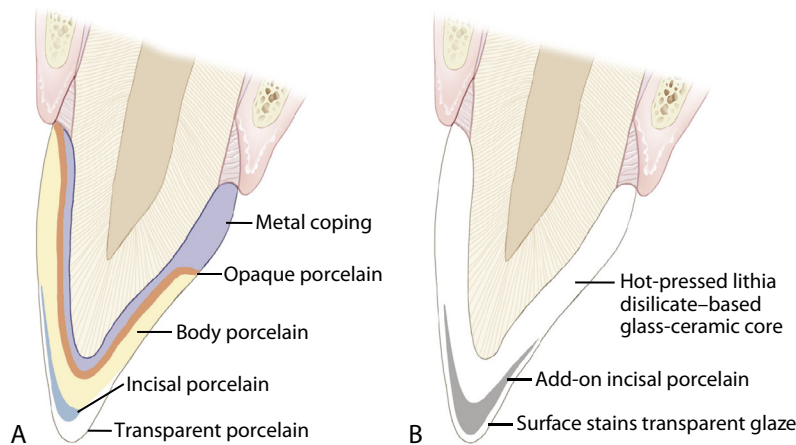
Metals and alloys, because of their mechanical properties, have been used for making indirect dental prosthetic restorations that include inlays/onlays, crowns and bridges, removable partial frameworks, and implants. A metal-ceramic or porcelain fused to metal (PFM) system is one in which esthetic ceramics are fused with metal substrates, where the metal functions as a coping,



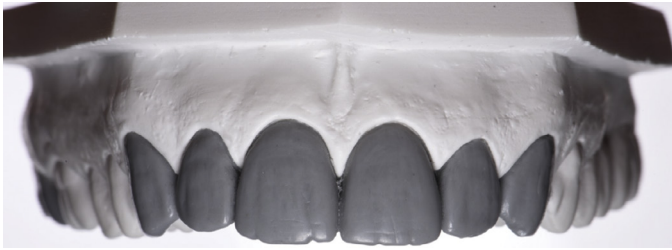
• **Figure 1-13** A set of complete removable dentures. (Courtesy Dr. Maged Abdelaal.)

supporting substructure (Figure 1-14, A). This allows the combination of metal's strength and ceramic's esthetics. Metals are crucial components of corrective orthodontic devices, helpful when aligning crooked teeth, and are used as a base for the placement of artificial plastic and ceramic teeth (partial denture framework) and for retentive features (clasps) in partial denture frameworks (Figure 1-12).

Ceramics, because of their esthetic appearance, have also been used to restore lost tooth structure partially (inlays/onlays) or completely (crowns) or to completely replace a missing tooth or teeth (multiple-unit fixed dental prostheses or bridges). However, because of the need for high fracture resistance and esthetic appeal, ceramic prostheses are constructed in multiple layers. The ceramic-ceramic or all-ceramic structure (Figure 1-14, B) is similar to metal-ceramic system, except that the metal coping



• **Figure 1-14** Schematic illustration of two crown prostheses. **A**, A metal-ceramic crown. The gray region is the metal coping. The remaining color regions represent various types of ceramics used to render esthetic appearance. **B**, A lithium disilicate all-ceramic crown. The thin metal coping is replaced with a thick ceramic core, and the multilayer ceramics are replaced with incisal porcelain.



• **Figure 1-15** Wax-up of anterior teeth on a gypsum cast. This approach is an important step in the decision-making process between the patient and the clinician for the esthetic outcome and surface stains.

is replaced with a thicker and tougher ceramic core ([Chapter 10, History of Dental Ceramics](#)).

Temporary and Provisional Restorative Materials

Temporary restorative materials, also known as *provisional restorative materials*, are products used for dental restorations that are not intended for moderate- or long-term applications. Indirect prostheses can take some time to be created and delivered, so temporary restorations are applied to protect the prepared tooth by covering any enamel, dentin, or pulp exposed to the buccal environment. These provisional restorations enable patients to speak and eat normally. Examples include cements for luting provisional prosthetic restorations; other restoratives used for fillings; orthodontic wires; and acrylic resins used when making provisional inlays, onlays, crowns, and fixed dental prostheses that span two or more tooth positions. Depending on the dental procedures needed, a temporary/provisional restoration may be in service for several months and up to a year.

Auxiliary Materials

Several different substances are needed to fabricate dental prostheses, appliances, and direct restorations. These substances, however, do not constitute part of these devices or restorations and, as a result, are called **auxiliary materials**. Among these are impression-making materials, gypsum cast materials to make dies, dental

waxes to make wax patterns ([Figure 1-15](#)) ([Chapter 13, Dental Waxes](#)), investments for metal casting ([Chapter 14, Investment materials](#)), and finishing and polishing abrasives for shaping and esthetics ([Chapter 16, Benefits of Finishing and Polishing Restorative Materials](#)). Additional materials are used in the auxiliary capacity but are not discussed as auxiliary materials in this book, such as plastic matrix for composites ([Chapter 5, Finishing and Polishing of Composites](#)), acid-etching solutions for enhancing bonding of direct restorations ([Chapter 6, Historical Background](#)), metal matrix for amalgam ([Chapter 8, Condensation](#)), and acrylic resins used to make customized impressions and bleaching trays ([Chapter 11, Resin Impression Trays and Tray Materials](#)).

Challenges of Dental Materials in the Oral Cavity

The overriding goal of dentistry is to maintain or improve the quality of life of the patient. This goal can be met by preventing disease, relieving pain, improving the efficiency of mastication, enhancing speech, and improving appearance after tooth and bone loss. However, dental restorations and appliances, compared with the natural dentition, endure additional challenges to withstand the oral environment. For example, as a replacement or addition to the tooth structure, they need to be retained in place. A strong and durable tooth/material interphase is desirable. They should resist repeated loading during occlusion. Both factors dictate the longevity of the restoration. They should be manipulated following very specific instructions in order to ensure their intraoral performance. The patient's acceptance of the restoration is determined by the esthetic appearance, cost, and the safety of the material. Evidence of material/tooth integration through the formation of hydroxyapatite also brings the possible need for tissue repair. These aspects are discussed in the following sections.

CRITICAL QUESTION

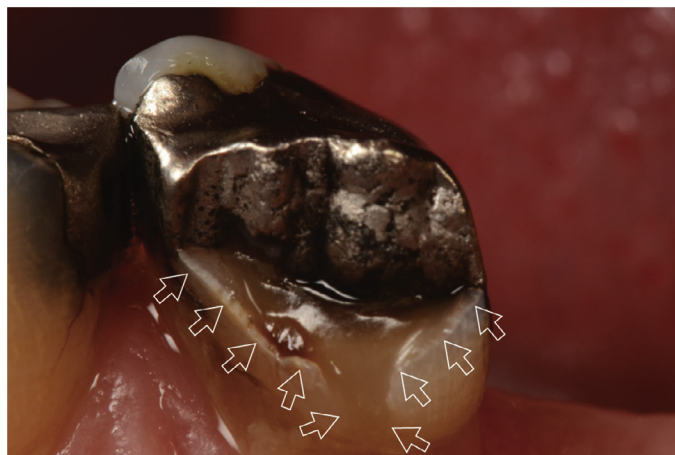
Retention of restorations can be achieved by mechanical or adhesive means; what are the advantages and disadvantages of these approaches?

Retention of Restorations

Retention, that is, the action of absorbing and continuing to hold a substance or material, is a highly relevant interfacial mechanism. Enamel and dentin, for instance, are two different biological materials held together by a graded interphase varying smoothly between the two adherent phases. Restorative materials must be secured to their intended location to be functional. However, there was no similar interphase available to hold restorative materials to the tooth structure in the beginning of dentistry.

The early approach was to remove the tooth structure, mainly to provide a location for macromechanical retention and create resistance to dislodgement of the restorations. The drawback with this approach is the common clinical observation of cusp fractures resulting from structural flaws of the tooth structure left by the surgical removal of decayed tissue (Figure 1-16), tooth pain caused by dentin hypersensitivity, and root canal therapy to remove hyperemic or necrotic pulp. Although restorations were retained satisfactorily by mechanical means, the nonadhesive dental materials of the time often left a discontinuity between the mechanically prepared surface and the restorative material used, which could lead to new carious lesions and pulp pathologies. This scenario led to the development of several pulp-protective philosophies and materials aimed at minimizing the penetration of bacteria and their by-products into the pulp, in addition to thermal insulation.

The acid-etching of enamel, combined with fluid resinous materials adopted in the 1950s, marked the first step toward generating a continuous interphase between the restoration and tooth structure. Technically, the process merely transforms macromechanical to micromechanical retention, with minimal tooth reduction beyond the removal of decayed tissue. Much later, etching of dentin with the same agent was accepted, and our knowledge of the dentin surface structure after etching expanded. New strategies of bonding, along with the introduction of new materials, have brought the idea of generating a stable and strong tooth/restoration interphase one step closer. Although progress has been made, the durability of this interphase remains a challenge. Adhesion and bonding are discussed in Chapter 6.



• **Figure 1-16** Fracture of the buccal cusp of a lower first premolar with an extensive intraorally serviced amalgam restoration. Open arrows delineate the area of fracture. Even though the amalgam remained firmly retained by the remaining tooth structure without the support of the lost cusp, it is considered a failed restoration and needs replacement.

Restoration Longevity in Terms of Mechanical Integrity

From both a patient's and a clinician's perspective, a restoration should last a lifetime. Although some materials are expected to last more than a lifetime, in a real-world scenario, the longevity of restorations is shorter than expected, especially for direct restorations. According to research, dentists spend more than 50% of their time replacing failed direct restorations. As a result, the longevity of dental biomaterials used in restorations is extremely relevant to the profession and to patients.

One of the major advances in the knowledge of dental materials and their manipulation began in 1919, when the U.S. Army requested the National Bureau of Standards (now known as the *National Institute of Standards and Technology* [NIST]) to establish specifications for the evaluation and selection of dental amalgams for use in federal service. The dental profession enthusiastically received these specifications, and similar specifications were subsequently requested for other dental materials. In 1928, dental research at the National Bureau of Standards was taken over by the American Dental Association (ADA).

Standards for dental materials have been developed to aid producers, users, and consumers in the evaluation of the safety and effectiveness of dental products. The ADA's Standards Committee on Dental Products (SCDP) develops specifications for dental materials, oral hygiene products, infection-control products, dental equipment, and dental instruments. Many countries have a dental standards organization that is charged with the development of test standards to ensure product reliability and safety. In addition, TC 106 of the International Organization for Standardization (ISO) develops international standards. These international standards often require information about composition; information about physical properties, as obtained by standard test methods; biocompatibility data; and data covering every provision of the official specification. More discussion of these standards is provided in Chapter 18, *Standardization of In Vitro Test Methods*.

From a material standpoint, meeting the specification for mechanical properties means the material possesses enough strength to withstand occlusal loading, but this does not guarantee durability. As mentioned earlier, the placement of dental materials, or restorations, over tooth structures leads to an interplay between solid materials and a series of linked and/or nonlinked, complex joints. The interfacial position at or within the tooth and the physical quality of the dental materials involved in this complex assembly have great effects on the longevity of the restoration. Other factors, such as the selection of materials, clinical indication, patient awareness of their oral hygiene, and manipulation of and compliance with the dental material manufacturer's guidelines, will undoubtedly affect the long-term clinical performance of the restorations. These aspects will be discussed in more detail in upcoming chapters.

Esthetic Appearance

Another important objective of dentistry is to restore or improve esthetics—the color and appearance of natural dentition—such as teeth bleaching with whitening agents. In recent decades, esthetic considerations in restorative and prosthetic materials have increasingly gained greater emphasis, making the development of general-purpose, technique-insensitive, tooth-colored, and color-stable restorative materials a mainstream of dental materials research. Resin-based composite (Chapter 5, *Classification of Composites*

by Clinical Use) and ceramics (Chapter 10, [Color Matching Ability and Aesthetic Qualities](#)) are the two most notable examples.

Even though esthetic materials that mimic natural dentition in color, texture, and reflectance allow the clinician to achieve outstanding esthetic and functional results, they also require strong artistic abilities. For example, knowledge of the underlying scientific principles of color and other optical effects on the appearance of the restorative material is essential in order to master esthetic results. Additionally, effective communication among the clinician, technician, and patient is important to achieve the proposed goal and avoid unrealistic expectations.

Safety of Dental Materials

Standards for dental materials have been developed to aid producers, users, and consumers in the evaluation of the safety and effectiveness of dental products. As mentioned previously, national dentistry standards/specifications have been implemented by the ADA's SCDP, and international standards have been implemented by the ISO's TC 106. Manufacturers can choose between testing their materials according to either national or international standards. However, for a manufacturer to market its product in certain European countries, a European Conformity (CE) marking must be obtained based on the product's ability to meet one or more national or international standards for performance and quality. A CE marking indicates that the product complies with European guidelines for health, safety, and environmental protection legislation.

The existence of material-evaluation standards does not prevent the manufacturing, marketing, purchase, or use of dental or medical devices that do not meet these standards. However, producers or marketers of products and devices are expected to meet the safety standards established for those products in the countries in which they are sold. Thus, a producer may be given premarket approval in the United States by the U.S. Food and Drug Administration (FDA) to sell a dental device or restorative material without that product being tested by the ADA or any other agency to determine whether the product is in accordance with the material's specifications. Nevertheless, these agencies are becoming increasingly dependent on one another to ensure that all products marketed worldwide are safe and effective.

For a dental material to be used in the oral cavity, this material should be harmless to all oral tissues and contain no toxic, leachable, or diffusible substance that can be absorbed into the circulatory system, causing systemic toxic responses, including teratogenic or carcinogenic effects. The material must also be free of agents that could elicit sensitization or an allergic response in a sensitized patient. These are considered general characteristics of biocompatibility.

Because safety is relative, no dental device (including restorative materials) is completely safe. The selection and use of dental devices or materials assume that the benefits will far outweigh the known biological risks. However, there is always the possibility that a patient will experience adverse effects from dental treatment. The conceptual aspects of biocompatibility, with specific emphasis on the solid and liquid materials of greatest relevance to dentistry, are presented in [Chapter 17](#).

Capability of Initiating Tissue Repair or Regeneration

Although restorative dental materials primarily focus on replacing missing tooth structure or missing teeth with synthetic materials, evidence shows that certain materials have triggered healing

or repair of tooth structure. For example, fluoride ions released in slightly acidic conditions, along with calcium phosphate, can promote the formation of hydroxyapatite within demineralized enamel matrix or become incorporated into the crystal lattice as fluorapatite, resulting in a lower solubility of enamel. The newly formed hydroxyapatite, however, lacks the structure and mechanical properties of natural enamel. As a result, the challenge is to develop biomimetic approaches in re-creating the hierarchical structure on the surface of the damaged enamel. Another example is when there is deep cavitation where dental pulp exposure has occurred, and a pulp capping agent is used. The response of the pulp to these materials is a biological healing process leading to the formation of reparative dentin that protects the remaining healthy pulp.

Understanding the underlying mechanisms of this "natural healing" biological process enables the clinician to pharmacologically trigger this event for promoting reparative dentine formation. As restorative dentistry is gradually transforming toward biology-driven repair strategies, replacement, and regeneration, the goal is regeneration of the entire tooth. The current progress in regenerative dentistry is presented in [Chapter 20, Regenerative Dentistry](#).

The Future Need for Dental Biomaterials

Future developments in dentistry and the need for optimal oral health care will dictate the future of dental materials science. Dentistry will continue to focus on the preservation and enhancement of oral health through the prevention of caries, periodontal disease, and their sequelae and the rehabilitation of missing, damaged, or destroyed hard and soft tissues. A cure for dental caries will have a dramatic impact on the use of restorative materials to restore form and function to teeth with cavitated lesions. However, there will still exist a continuous need to repair or restore time-dependent failure or degradation of restorations and a need for the treatment of noncarious-related issues. As a result, deciding which materials to use for a given clinical condition or situation will depend on the known benefits of each treatment choice compared with the known risks.

Because a cure for caries and the development of processes for root or tooth regeneration are probably several decades away, most of the restorative materials employed today will likely remain in use for the foreseeable future. Materials like dental amalgam ([Chapter 8, Safety of Amalgam Restorations](#)), for example, have made reliable restorations for centuries. The use of amalgam has been declining rapidly, not because there are more durable and technique-insensitive restorative materials available in the market but because of concerns regarding the impact of mercury release into the environment. Furthermore, the world has moved into an era of high esthetic demand at the expense of durability and cost. In contrast to the treatment for dental caries, the demand for esthetic enhancement will continue well into the future. Development and research for direct restorative biomaterials that are less technique-sensitive, especially the existing esthetic resin-based composite brands, still have great room for improvement. In addition, strategies that aim to increase the hardness, toughness and resistance to wear, and impact of these materials is relevant to the field. An interesting approach relies on creating composites with tailored microstructures, or bio-inspired platelet-reinforced composites created by magnetic manipulation of alumina platelets.

The benefits of caries prevention have led to a reduction in the need for complete and removable dentures. Minimally invasive concepts have led to the sealing of defective or leaking restorations with preventive resins rather than continuing to use more

destructive replacement procedures. Thus, the development of effective bio-inspired remineralizing agents for acid-damaged enamel and dentin repair and the development of smart materials that lead to self-repair of defective joints or of a material's internal flaws, as well as dental pulp regeneration, will be critical challenges to the future of dental materials. In addition, the need for replacement of restorations should decrease over the next several decades, in lieu of the minimally invasive philosophy. However, this reduction will be offset by the increased demand for esthetic restorations (discussed in [Chapter 20, Biomaterials](#)).

CRITICAL QUESTION

Which factors determine when dental material products become obsolete?

Technology has advanced tremendously over the past 40 years, resulting in innovations such as laser applications, imaging procedures, three-dimensional (3-D) printing technology, low-shrinkage composites, smart ceramics, and minimally invasive dental procedures, which have generated benefits for several fields. Computer-aided design/computer-aided manufacturing (CAD-CAM) technology for making indirect restorations, for example, has reduced the demand for both impression materials and some indirect auxiliary materials that were used by laboratory technicians to fabricate indirect prostheses (discussed in [Chapter 15, Digital Impressions and Prototyping Tools](#)).

Subsequently, one question has accompanied the dental profession for centuries: When does a restorative material become obsolete? For example, silicate cement ([Chapter 7, History of Dental Cements](#)) was used to restore anterior esthetic restorations because the color perception resembled tooth structure, and there was a serendipitous ability to release fluoride. Although the latter is beneficial in preventing recurrent caries, fluoride release occurs at the expense of surface degradation, discoloration, and marginal breakdown over time, resulting in defective and stained margins ([Figure 1-17](#)) and loss of anatomical contour. Furthermore, more durable resin-based composites and improved micromechanical bonding procedures made silicate cements virtually obsolete by the mid-1970s.



• **Figure 1-17** Anterior class III silicate cement restorations exhibiting severe surface degradation, marginal staining, and general discoloration.

Therefore we can conclude that some restorative materials became obsolete for the following reasons: (1) their drawbacks overall far outweighed their known advantages; (2) material degradation led to undesirable margin adaptation and esthetics; (3) metallic appearance was generally unacceptable to patients; (4) alternative restoratives exhibit superior performance, mimic the physiology of the tooth, and are less technique-sensitive; (5) alternative materials led to cheaper treatment for patients; and/or (6) improvements in material microstructure occur as a result of technological advances. In short, restorative materials become obsolete when an alternative material is able to provide a better balance among all the previously mentioned diverse requirements and expectations.

Organization of the Book

In 1936, Dr. Skinner, the author of the first edition of this book, expressed significant concerns regarding the need for knowledge of dental materials science in the following statement:

Unfortunately, there are too many unscrupulous dental manufacturers who make impossible claims for inferior products, thus deceiving the dentist. There have been actual cases of highly advertised dental materials, which have been made extremely popular among dentists simply by clever advertising methods, whereas careful laboratory tests have shown products to be distinctly inferior. The well-informed dentist will be able to discriminate between fact and propaganda and will refuse to be duped in this manner.

He emphasized the need for the principles of physics and chemistry to be applied in restorative dentistry in a similar manner as they were applied to structural engineering. Although there have been many technological advancements since 1936 that improved the quality of dental materials, a challenge remains for end users to critically evaluate the claims made for the performance of dental materials and to carefully relate these claims to well-established physical principles for specific classes of materials. The current era of evidence-based dentistry is consistent with our aims of presenting fundamental principles of materials and understanding cause-and-effect relationships that allow us to predict, with reasonable certainty, the time-dependent behavior of dental materials.

To achieve these aims, this book is organized into five parts: (I) General Classes and Properties of Dental Materials; (II) Direct Restorative Materials; (III) Indirect Restorative and Prosthetic Materials; (IV) Fabrication of Prostheses; and (V) Assessing Dental Restorations.

Following the overview of dental materials in this chapter, Part I focuses on the structure and properties of materials. [Chapter 2](#) explains how the molecular or crystalline structure determines the classes of materials and renders each class its unique properties. This chapter also discusses the origin of adhesion, an important feature of dental restorations. [Chapter 3](#) discusses the physical and chemical properties relevant to dental applications, and [Chapter 4](#) examines the mechanical properties of dental materials.

The chapters in Part II focus on direct restorative materials, including resin-based composites ([Chapter 5](#)), bonding agents ([Chapter 6](#)), dental cements ([Chapter 7](#)), and metallic-based restorations ([Chapter 8](#)). As stated earlier, these materials share the same feature of being manipulated chairside and applied to the oral cavity before they reach their full functional state. Therefore preventive materials are discussed with direct restorative materials.

The chapters in Part III discuss the use of indirect restorative materials, such as dental casting alloys and wrought metals

(Chapter 9), ceramic-based materials (Chapter 10), denture-base resins (Chapter 11), and dental implants (Chapter 12).

Chapter 13 through 16 in Part IV describe the materials and technologies needed to fabricate indirect prostheses. Chapter 13 discusses auxiliary materials, which include impression materials, gypsum products, and dental waxes, which are used to fabricate the wax patterns needed for final prostheses. The process of making metal castings using the lost wax method is discussed in Chapter 14, and Chapter 15 discusses the use of digital technology for making dental prostheses without using traditional auxiliary materials but instead relying on digital imaging and CAD-CAM technology. Finally, all restorations, direct or indirect, require certain degrees of surface modification to improve their clinical performance. The procedures and the essential instruments used for finishing and polishing restorations are discussed in Chapter 16.

The goal of dentistry is to maintain or improve the quality of life of the patient. The restorations involved must prevent disease, relieve pain, improve the efficiency of mastication, enhance speech, improve appearance, and most importantly, last for a long time. Part V aims to address the question of how we assess restorations. As stated, all materials undergo some sort of interaction with the

oral tissue. The biological considerations, known as *biocompatibility*, are covered in Chapter 17. In vitro testing is conducted by subjecting a material made in a certain configuration to a known external factor (or factors) in a well-defined condition and recording the material's response to such factors. The significance of in vitro testing is discussed in Chapter 18. Clinical evaluations of a dental restoration represent a different level of assessment for restorations. Chapter 19 discusses the components of clinical studies, using one to illustrate how variables can be collected from the study. Finally, although new materials that address the particular needs of restorative dentistry are emerging and alternative treatment philosophies are being adopted, the advancement of new technologies in other disciplines has benefited dental materials science in a variety of ways. Chapter 20 analyzes potential future technologies in dentistry and describes both recently emerged technologies and those anticipated in the coming decades.

Acknowledgment

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2

Structure of Matter, General Classes of Material and Principles of Adhesion

OUTLINE

Interaction Between Two Atoms

Types of Bonding

Atomic Arrangement

Metals

Ceramics

Polymers

Composite Materials

Adhesion and Bonding

Bonding to Tooth Structure

KEY TERMS

Adhesion An attraction between two contacting surfaces promoted by the interfacial force of attraction between the molecules or atoms of two different species; adhesion may occur as chemical adhesion, mechanical adhesion (structural interlocking), or a combination of both.

Adhesive and adherend Substance that promotes adhesion of one substance or material to another. An adherend is a material substrate bonded to another material by means of an adhesive.

Alloy and alloy system An alloy is a crystalline solid with metallic properties that is composed of two or more elements, at least one of which is a metal, and all of which are mutually soluble in the molten state. Alloy systems are all possible alloyed combinations of two or more elements, at least one of which is a metal. For example, the binary gold-silver system includes all possible alloys of gold and silver, varying from 100% gold and 0% silver to 100% silver and 0% gold.

Bonding The action of joining objects or particles together by means of adhesive or force of attraction.

Ceramic Solid-phase compounds of metallic and nonmetallic elements.

Cohesion Bonding between molecules or atoms of the same species.

Composite A material made of two or more constituent components with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components.

Contact angle Angle of intersection between a liquid and a surface of a solid that is measured from the solid surface through the liquid to the liquid/vapor tangent line originating at the terminus of the liquid/solid interface; used as a measure of wettability, whereby no wetting occurs at a contact angle of 180° , and complete wetting occurs at an angle of 0° .

Copolymer Polymer made of two or more types of monomers. A *random copolymer* is when there is no sequential order of monomer types along the polymer chain. A *block copolymer* is when groups of each type of monomer appear in the same

polymer chain. A *graft or branched copolymer* is when a sequence of one type of mer unit is grafted onto the backbone of a second type of monomer to form a branched structure.

Crosslink A difunctional or multifunctional monomer that forms a link between two growing polymer chains during polymerization that results in a three-dimensional interconnected polymer network.

Curing Chemical reaction in which low-molecular-weight monomers are converted into higher-molecular-weight materials through polymerization to attain desired properties.

Elastic recovery The shape of objects changes under an applied force. When the force is removed, the object will recover to its original shape instantly if it is an *elastic* solid, or the recovery process occurs over a period of time if it is a *viscoelastic* material. The greater the viscous nature of a material, the less complete the recovery.

Glass-transition temperature (T_g) (1) The temperature above which a sharp increase in the thermal expansion coefficient occurs, indicating increased molecular mobility. (2) The temperature at which macromolecule molecular motion begins to force the polymer chains apart. Thus polymeric materials soften when heated above this temperature.

Grain and grain boundary A grain is a single crystal in the microstructure of a metal. Metals and alloys are solids consisting of many individual grains, and the interface between adjacent grains is the grain boundary.

Metal (1) An element or alloy whose atoms readily lose electrons to form positively charged ions. (2) A metallic material composed of one or more elements that is opaque, ductile, relatively malleable, a good conductor of electricity, a good thermal conductor, and usually lustrous when light is reflected from its polished surface.

Microstructure Structural features of a surface, including grains, grain boundaries, phases, and defects, such as porosity, revealed by microscopic imaging of the chemically or electrolytically etched surface of a flat, polished specimen.

Micromechanical bonding Retention associated with an adhesive penetrating a roughened adherend surface.

Monomer and mer A monomer is a chemical compound that is capable of reacting to form a polymer; each monomer becomes a *mer* of a polymer.

Phase and phase diagram (constitution diagram) A graph of equilibrium phases and solubility limits for an alloy system as a function of composition and temperature.

Polymer Large molecules (a.k.a. *macromolecules*) formed by the union of many simple repeating units (mers); the chemical process is known as *polymerization*.

Primary bond Bonding between atoms that include ionic, covalent, and metallic bonds.

Resin or synthetic resin Blend of monomers and/or macromolecules with other components, which form a material with a set of useful properties.

Solid solution (metallic) A solid crystalline phase containing two or more elements, at least one of which is a metal and whose atoms share the same crystal lattice.

Strain Magnitude of deformation (stretching, compression, or shear) occurring in response to an applied force.

Stress The perpendicularly directed force, exerted as pressure or tension, on a material that causes the object to deform (strain), measured in units of force per unit area.

Surface energy The excess energy of attraction that the surface of a material (liquid and solid) has compared with the bulk of the material because molecules or atoms at the surface are

not surrounded by their fellows as those in the bulk. It can be treated as the work (energy) required to build an area of a particular surface and has the unit of mN/m^2 .

Surface tension The tendency of fluid surfaces to contract to the smallest surface area by an inward force caused by the imbalance of mutual attraction between molecules on the liquid surface. The very inward force also keeps the molecules of the surface constantly under tension. The cohesive force keeping molecules bonded on the surface is known as the *surface tension* of the liquid, with the unit of mN/m .

Thermoplastic polymer Macromolecule material made of linear and/or branched chains that softens when heated above the glass-transition temperature (T_g); it can then be molded to a new shape and cooled below the T_g to retain the new configuration.

Thermoset polymer Polymeric material that retains a crosslinked structure during polymerization; the acquired structure results in a rigid polymer that, upon heating, does not soften enough to be molded to a new configuration.

van der Waals forces Short-range force of physical attraction that promotes adhesion between molecules of liquids or molecular crystals. Also known as *secondary bond*.

Wetting and wetting agent Wetting is the ability of a liquid to maintain contact with a solid surface; it reflects the intermolecular interactions when the two are brought in intimate contact. A wetting agent is a surface-active substance that can be applied to a solid substrate to reduce the surface tension of the liquid to be placed on the solid; the purpose is to promote wetting or adhesion.

All matter is composed of indivisible particles called *atoms*, the smallest size of particles having properties identical to those of bulk material. The commonly accepted structure of atoms consists of three subatomic particles, a negatively charged electron, a positively charged proton, and an electrically neutral neutron, as depicted in the electron cloud model of a nitrogen atom (Figure 2-1). The nucleus contains a mix of protons and neutrons, except for the hydrogen atoms, where there are no neutrons. Neutrons and protons are held together by nuclear force that is stronger than the repulsion forces between protons. Nuclear force only acts at an extremely short distance ($\cong 1 \times 10^{-15}$ m) and does not affect the electromagnetic attraction. The electrons of an atom exist in different clouds at the various energy levels (shells). An atom becomes a negative ion when it gains an electron(s) or a positive ion when

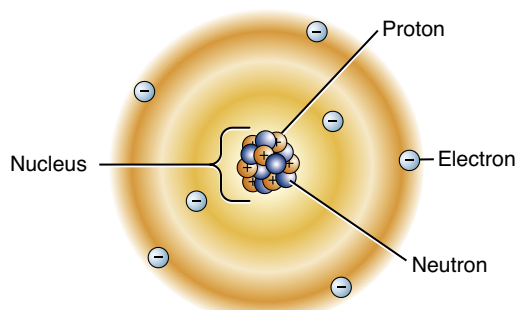
it loses an electron(s). The number of electrons in the shells of the cloud dictates the property of the matter made of that group of atoms. These electrons are also called *valence electrons*.

CRITICAL QUESTION

When the state of material (vapor, liquid, and solid) changes, what happens between atoms or molecules that make up the material?

Two or more atoms can bond together and form an electrically neutral entity called a *molecule*. The attraction between atoms within a molecule is strong, whereas the attractions between molecules are weaker. These attractions result in materials we can see and touch. Consider water as an example. Chemically, the basic unit of water is a molecule made of two hydrogen atoms and one oxygen atom. If each molecule attains a kinetic energy that is higher than the attraction between these molecules, they appear in vapor form. Kinetic energy is what allows molecules of known mass to maintain a constant in motion. As the surrounding temperature decreases, the level of kinetic energy within individual molecules decreases, and the attraction between them becomes more prominent so that they condense to liquid form. Further cooling yields a solid called *ice*, where the kinetic energy is so low that the molecules are immobilized by attraction forces among them.

The transformation between vapor, liquid, and solid is called *change of state*, which is an example of how the attraction between molecules and the environment affects the behavior of a material as we observe it. The focus of this chapter will be on how the atomic and molecular attractions shape the four classes of materials used in dentistry, namely, **metals**, **ceramics**, **polymers**, and



• **Figure 2-1** Electron-cloud model of a nitrogen atom. The neutrons (blue spheres) and protons (orange spheres with "+") occupy a dense central region called the nucleus. The orange cloud formation illustrates the trace of electrons (spheres with "-") as they move around the nucleus.

composites, and affect their behavior in their respective applications. Finally, we will discuss how we can use these **bonding** mechanisms to our advantage.

Interaction Between Two Atoms

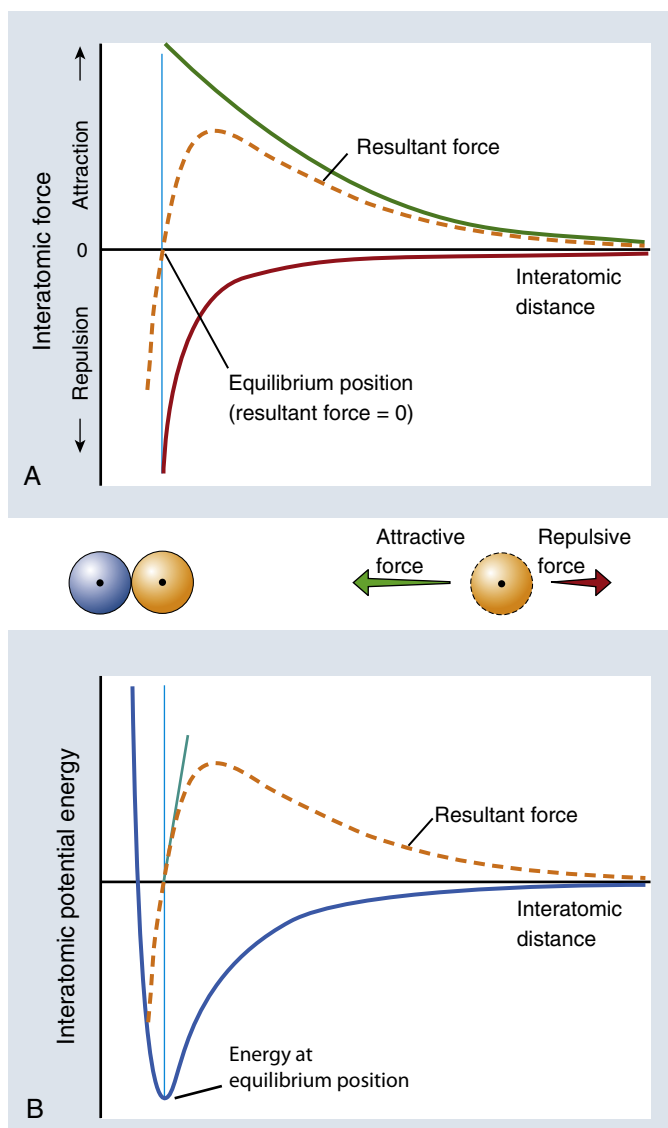
We can treat each atom as a discrete entity with definite boundaries and volume established by the electromagnetic fields of the electrons. When two atoms interact with each other in space, they feel an attraction force from the interaction of the opposite-charged particles of either atom and an expulsion force from the interaction of the similar-charged particles of either atom. At a large distance, the interaction between atoms is negligible (Figure 2-2, A). In Figure 2-2, A, the repulsion and attraction forces are plotted as a function of the interatomic spacing, which is the distance between the centers of the cores of the atoms. When the atoms come close to each other, both forces increase as the distance between the atoms decreases. Initially, the force of attraction increases faster than the force of repulsion. The repulsion force is a short-range force compared with the attractive force that becomes noticed at a closer range. Later, the force of repulsion increases much more than the force of attraction as the atoms get closer. The resultant force, which is the sum of attraction and repulsion forces, increases initially as attraction force when the two atoms get close. As the repulsion force increases, the resultant attractive force, after reaching a peak, starts to decline. It then reaches a state of equilibrium when the valence electron shells of the two atoms keep the atoms from getting closer. At the state of equilibrium, there is no net resultant force (Figure 2-2, A). In other words, the atoms have reached a stable state. Before the atoms reach equilibrium, we can treat the resultant force as the force needed to keep them apart at that distance. After equilibrium, the negative resultant force means that external force is needed to push the atoms closer. There is a great deal of repulsion to overcome. Depending on the number of valence electrons and species of atoms involved, there are three types of interaction between atoms when equilibrium is reached.

Bond Distance

Regardless of the type of structure in the solid state, there is a limiting factor that prevents the atoms or molecules from approaching each other too closely. The position at which both attraction and repulsion forces are equal in magnitude (but opposite in direction) is considered the equilibrium position of the atoms (Figure 2-2, A). The interatomic distance at equilibrium represents the sum of the radii of the two adjacent atoms.

Bond Energy

Because the conditions of equilibrium are usually described in terms of energy rather than interatomic forces, the relationships in Figure 2-2, A can be logically explained in terms of interatomic energy, which is also known as *bond energy* or *potential energy*. Energy is defined as the product of force and distance. Integration of the interatomic force (dashed line in Figure 2-2, A) over the interatomic distance yields the interatomic energy (solid line in Figure 2-2, B). In contrast with the resultant force, the bond energy can be treated as the energy needed to keep two atoms apart. Initially, the bond energy decreases gradually as two atoms come closer together. As the resultant attractive force passes the peak and begins to decline rapidly, the bond energy also decreases steeply (Figure 2-2, B).



• **Figure 2-2** Interaction between two atoms. The blue atom is stationary, and the orange atom is moving toward or away from the blue atom. The bond distance is the distance between the core center of the two atoms. **A**, Relation of interatomic forces to interatomic distance. The resultant force (—) is the sum of attraction (—) and repulsion (—) forces. At the equilibrium position (—), either a negative (repulsive) or a positive (attractive) force is required to move the atom out of its equilibrium position. **B**, Integration of the resultant force (—) shown in **A** over the interatomic distance yields the interatomic energy (—). Note that the potential energy is at minimum when equilibrium (—) is reached. The tangent of the resultant force at equilibrium (—) is the slope of the curve.

The bond energy reaches a minimum when the resultant force becomes zero. Thereafter, the energy increases rapidly because the resultant force becomes repulsive and increases rapidly with little change in interatomic distance. The minimum energy corresponds to the condition of equilibrium and defines the equilibrium interatomic distance.

Influence of Interatomic Bond

The atoms are in a constant state of vibration, and the average amplitude is dependent on the temperature; the higher the

temperature, the greater is the amplitude and, consequently, the greater is the kinetic energy. At a certain temperature, the minimal energy required to maintain equilibrium is denoted by the bottom of the trough in **Figure 2-2, B**. As the temperature increases, the amplitude of the atomic (or molecular) vibration increases. It follows also that the mean interatomic distance increases (**Figure 2-3**), as does the internal energy. The overall effect is the phenomenon known as *thermal expansion*.

As the temperature increases from T_0 to T_5 in **Figure 2-3, A**, the mean increase in interatomic distance is less with the deeper energy trough (**Figure 2-3, A**) than that in the shallower energy trough (**Figure 2-3, B**). This means that the linear coefficient of thermal expansion (α) of materials with similar atomic or molecular structures tends to be inversely proportional to the melting temperature. If the temperature continues to increase, the increase in interatomic distance will result in a change of state, where solid melts to a liquid, and liquid subsequently vaporizes to gas. For a solid with lower potential energy (i.e., a deeper trough depth) (**Figure 2-3, A**), greater amounts of kinetic energy are required to achieve melting and boiling, which corresponds to higher melting and boiling temperatures.

As shown in **Figure 2-2, A**, the net force on the atoms at the equilibrium distance is zero, but small displacements, as in an

increased bond distance, result in rapidly increasing forces to maintain the equilibrium distance. The magnitude of this force needed to maintain the displacement is commonly referred to as the *elastic modulus* or *stiffness* of the material, and this property will be discussed in detail in **Chapter 4, Stress-Strain Properties**. The stiffness or elastic modulus of the material is proportional to the rate of change of the force with a change in displacement that is measured by the slope of the net-force curve drawn from the equilibrium (**Figure 2-2, B**). A greater slope of the force curve implies a narrower, deeper trough in the energy curve (**Figure 2-3, A**). Hence, a high melting point is usually accompanied by a greater stiffness.

The preceding principles represent generalities, and exceptions do occur. Nevertheless, they allow one to estimate the influence of temperature on the properties of most of the dental materials discussed in subsequent chapters.

Types of Bonding

The preceding discussion establishes the role of bonding in the change of state and interatomic bond energy of the thermal and mechanical properties. When the atoms are in the equilibrium state with the neighboring atoms, they establish different types of bonds according to the valence of their electrons. The electron structure of an atom is relatively stable if it has eight electrons in its outer valence shell, as noble gases do, except for helium, which has only two electrons. Other atoms must lose, acquire, or share electrons with yet other atoms to achieve a stable configuration—that is, eight electrons in the outer shell. These processes produce strong **primary bonds** between atoms. Intermolecular bonds, on the other hand, rely on dipole forces induced by nonuniform distribution of electrons within the molecule. These are often weaker and are called *secondary bonds*.

Primary Bonds

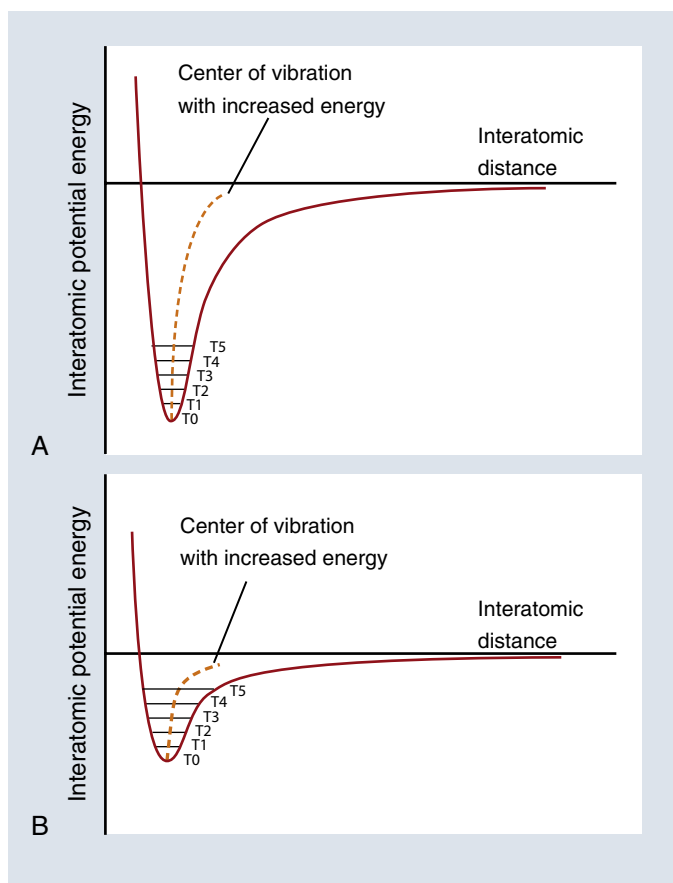
The formation of primary bonds depends on the atomic structures and their tendency to assume a stable configuration. The strength of these bonds and their ability to re-form after breakage determine the physical properties of a material. Primary atomic bonds (**Figure 2-4**), also called *chemical bonds*, may be of three different types: (1) ionic, (2) covalent, and (3) metallic.

Ionic Bonds

The classic example of ionic bonding is the bond between the Na^+ and Cl^- of sodium chloride (**Figure 2-4, A**). Because the sodium atom contains one valence electron in its outer shell and the chlorine atom has seven electrons in its outer shell, the transfer of the sodium valence electron to the chlorine atom results in the stable compound Na^+Cl^- . In dentistry, ionic bonding exists in some dental materials, such as in gypsum and phosphate-based cements.

Covalent Bonds

A covalent bond is a chemical bond that involves the sharing of electron pairs between atoms. **Figure 2-4, B** shows that the fluorine molecule shares a pair of electrons. By virtue of sharing electrons, the two atoms are held together by covalent bonds to form a molecule that is sufficiently stable and electrically neutral in a definite arrangement. The hydrogen molecule, H_2 , exemplifies covalent bonding. The single valence electron in each hydrogen atom is shared with that of the other combining atom, and the valence shells become stable. Covalent bonding occurs in many organic



• **Figure 2-3** Thermal energy and bond energy. As the temperature rises from T_0 to T_5 , the interatomic distance increases. For the solid with a deeper potential energy trough (**A**), the actual increase in distance is less than that of the solid with a shallower potential energy trough (**B**). Therefore less thermal expansion and a higher melting temperature are expected for (**A**). In addition, a high melting temperature usually is accompanied by a greater stiffness.

compounds, such as dental resins, where they link to form the backbone structure of hydrocarbon chains.

Metallic Bonds

The third type of primary atomic interaction is the metallic bond (Figure 2-4, C). It is found in elements with one, two, or three valence electrons. The outer-shell valence electrons can be removed easily from metallic atoms and form positive ions. The free valence electrons can move about in the metal space lattice to form what is sometimes described as an electron “cloud” or “gas.” The electromagnetic attraction between the electron cloud and the positive ions in the lattice provides the force that bonds the metal atoms together as a solid. The free electrons give the metal its characteristically high thermal and electrical conductivity. These electrons absorb light energy, so all metals are opaque to transmitted light. The metallic bonds are also responsible for the ability of plastic deformation of metals. *Plastic deformation* means a material can be reshaped by force without fracture. The free electrons can move through the lattice, whereas their plastic deformability is associated with slip along crystal planes. During slip deformation, electrons easily regroup to retain the cohesive nature of the metal.

Combination of Primary Bonds

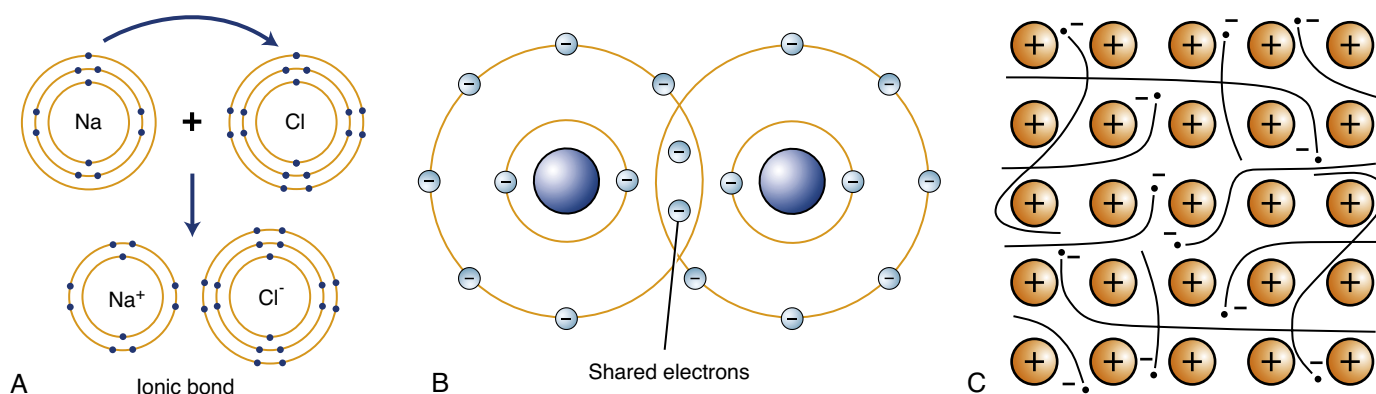
Although we can describe the three primary bonds separately, it is also possible to find more than one type of primary bond existing in one material. Consider calcium sulfate (CaSO_4), the main ingredient of gypsum products (Chapter 13, Gypsum Products), as an example. In the sulfate ion (SO_4^{2-}), the sulfur and oxygen atoms are held together covalently but are short two electrons. Calcium has two electrons in the outer orbit, which are easily removed and transferred to the SO_4 . The result is a Ca^{2+} ion with attraction for an SO_4^{2-} ion.

Secondary Bonds

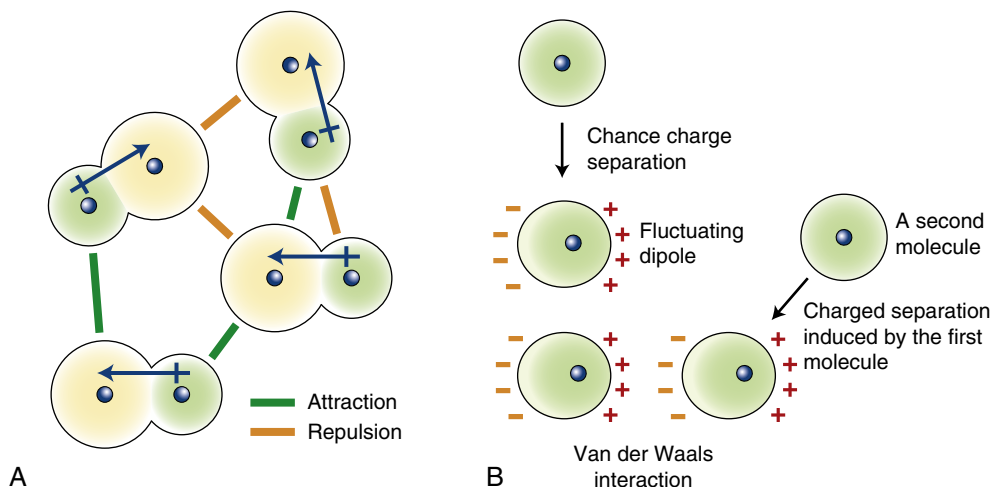
In contrast with primary bonds, secondary bonds do not share electrons between molecules. Instead, the asymmetrical distribution of electrons within each molecule induces dipole forces that attract molecules together.

Van der Waals Forces

Van der Waals forces of attraction arise from dipole attractions (Figure 2-5). In the case of polar molecules, dipoles are induced by an unequal sharing of electrons (Figure 2-5, A). In the case of



• **Figure 2-4** Primary bonds. **A**, Ionic bond, characterized by electron transfer from one element (Na) to another (Cl). **B**, Covalent bond, characterized by electron sharing and very precise bond orientations. Fluorine molecules (F_2) share one pair of electrons. **C**, Metallic bond, characterized by electron sharing and the formation of a “cloud” of electrons that bonds to the positively charged nucleus in a lattice.

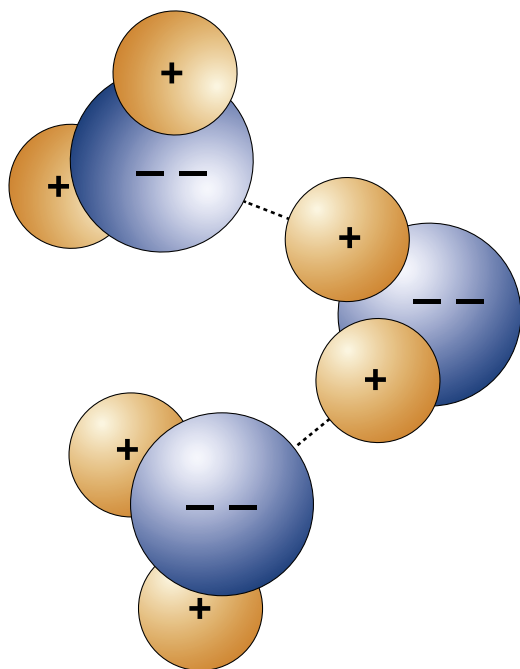


• **Figure 2-5** Van der Waals forces by dipole attraction. **A**, Polar compound; the attraction and repulsion between molecules are induced by a permanent dipole moment resulting from asymmetrical electron distribution within the molecule. **B**, Nonpolar compound; a temporary dipole (fluctuating dipole) occurs when the symmetrical distribution of electrons in a molecule becomes asymmetrical temporarily; it then attracts the dipole to adjacent molecules, resulting in the eventual interaction.

nonpolar molecules, the random movement of electrons within the molecule creates fluctuating dipoles (Figure 2-5, B). Dipoles generated within these molecules will attract other similar dipoles. Such interatomic forces are quite weak compared with the primary bonds.

Hydrogen Bond

The hydrogen bond is a special case of dipole attraction of polar compounds. It can be understood by studying a water molecule (Figure 2-6). Attached to the oxygen atom are two hydrogen atoms. These bonds are covalent. Therefore the protons of the hydrogen atoms pointing away from the oxygen atom are not shielded efficiently by the electrons. They become positively charged. On the opposite side of the water molecule, the electrons that fill the outer shell of the oxygen provide a negative charge. The positive hydrogen nucleus is attracted to the unshared electrons of



• **Figure 2-6** Hydrogen-bond formation between water molecules. The polar water molecule bonds to adjacent water molecules via an H (orange) O (blue) interaction between molecules.

neighboring water molecules. This type of bond is called a *hydrogen bridge*. Polarity of this nature is important in accounting for the intermolecular reactions in many organic compounds—for example, the sorption of water by synthetic dental resins.

Atomic Arrangement

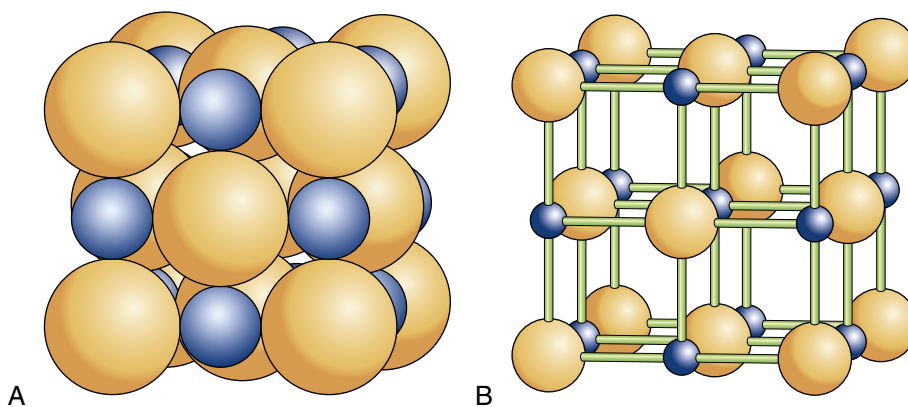
All materials we use consist of trillions of atoms. As described earlier, they are attracted to each other and retain a physical appearance. The question is in which configuration they are held together. In 1665, Robert Hooke explained crystal shapes in terms of the packing of their component parts, like stacking musket balls in piles. This is an exact model of the atomic structure of many familiar metals, with each ball representing an atom.

In the solid state, atoms combine in a manner that ensures minimal internal energy and the most efficient packing of atoms. For example, sodium and chlorine share one electron at the atomic scale. In the solid state, like grains of salt, they do not exist in individual pairs; in fact, each sodium ion is attracted to six chlorine ions, and vice versa (Figure 2-7). They form a regularly spaced configuration (long-range repetitive space lattice) known as a *crystal*. A space lattice can be defined as any arrangement of atoms in space in which every atom is situated similarly to every other atom.

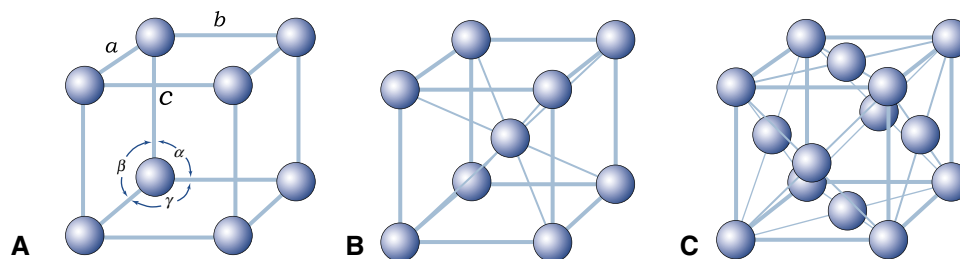
There are structures where regularly spaced configurations do not occur in the solid state. For example, the molecules of some of the waxes used by a dentist or laboratory technician are distributed at random when solidified. This noncrystalline formation is also known as an *amorphous structure*.

Crystalline Structure

There are 14 possible lattice types. The type of space lattice is defined by the length of the three unit cell edges (a -, b -, and c -axes) and the angles (α , β , and γ) between the edges. The simplest and most regular lattice is a cubic, as shown in Figure 2-8, A; it is characterized by axes that are all equal length and meet at 90° angles, representing the smallest repetitive volume of a crystal, which is called a *unit cell*. Each sphere represents the positions of the atoms. Their positions are located at the points of intersection of three planes, each plane (surface of the cube) being perpendicular to the other two planes. These planes are often referred to as *crystal planes*. However, the simple cubic arrangements shown in Figure 2-8, A, is hypothetical because it leaves enough space to fit additional atoms per unit cell.



• **Figure 2-7** The atomic arrangement of table salt. **A**, Sphere model showing that atoms are actually closely packed together. **B**, Ball-and-stick model displaying the three-dimensional position of the atoms and bonds between them. The orange spheres are chlorine ions, and the blue spheres are sodium ions.



• **Figure 2-8** Unit cells of the cubic space lattices. **A**, Simple cubic. **B**, Body-centered cubic. **C**, Face-centered cubic.

Most metals used in dentistry belong to the cubic system. For example, iron at room temperature has an atom at each corner of the cube and another atom at the body center of the cube (Figure 2-7, **B**). This crystal form is called a *body-centered cubic (BCC) cell*. Copper, on the other hand, has additional atoms at the center of each face of the unit cell but none at the center of the cube. This form is called a *face-centered cubic (FCC) cell* (Figure 2-7, **C**). At first glance of Figure 2-7, **B**, one may think NaCl retains a simple cubic crystal if we consider that sodium and chlorine occupy the same lattice. That is incorrect. Sodium atoms occupy an FCC lattice, and chlorine atoms occupy their own FCC lattice. The two FCC lattices interpenetrate to form the final lattice. Other types of space lattices of dental interest are shown in Figure 2-9. The hexagonal close-packed arrangement (Figure 2-9, **G**) observed in titanium, zinc, and zirconium has become an important crystalline structure in dentistry. Note that each unit cell consists of three layers of atoms, and the base, being hexagonal, has a 120° edge.

All metallic-based dental materials are crystalline. Some pure ceramics, such as alumina and zirconia core materials, are entirely crystalline.

Noncrystalline Structure

Glass is a typical noncrystalline solid of SiO_2 because its atoms tend to be arranged in nonrepeating units (Figure 2-10). The ordered arrangement of the glass is locally interspersed with a considerable number of disordered units. Because this arrangement is also typical of liquids, such solids are sometimes called *supercooled liquids*. Because of the complexity of the physical configuration of polymer chains, the molecules of resins are not favored to arrange in orderly, repeating patterns. Therefore polymer-based materials used in dentistry are usually noncrystalline.

The structural arrangements of the noncrystalline solids do not represent such low internal energies as do crystalline arrangements of the same atoms and molecules. Noncrystalline solids do not have a definite melting temperature but, rather, gradually soften as the temperature is raised. The temperature at which there is an abrupt increase in the thermal expansion coefficient, indicating increased molecular mobility, is called the **glass-transition temperature** (T_g) (Figure 2-11); it is characteristic of the glassy structure. Below T_g , the material loses its fluid characteristics and gains significant resistance to shear deformation. When set, synthetic dental resins are examples of materials that often have glassy structures, with T_g greater than body temperature.

Many dental materials often consist of a noncrystalline glassy matrix and crystalline inclusions (filler phase). Crystalline inclusions provide desired properties, including color, opacity, increased thermal expansion coefficients, and in some dental ceramics,

increased radiopacity. The filler phase of resin-based composites (Chapter 5, **Fillers**), on the other hand, can be crystalline, such as quartz particles or noncrystalline glass spheres.

Diffusion

When we place a drop of ink in a bowl of water, we observe the spread of the ink in the water. It will eventually disperse throughout the entire body of the water. This process is called *diffusion*. The same process also occurs within solid materials but at a substantially slower rate. An understanding of diffusion in a solid requires two new concepts.

First, the atoms in a space lattice, as previously described, are constantly in vibration about their centers. However, the atoms in the material do not all possess the same level of energy. Rather, there is a distribution of atoms with energy that varies from very low to high, with the average energy at equilibrium. If the energy possessed by an atom exceeds the bond energy, it can move to another position in the lattice.

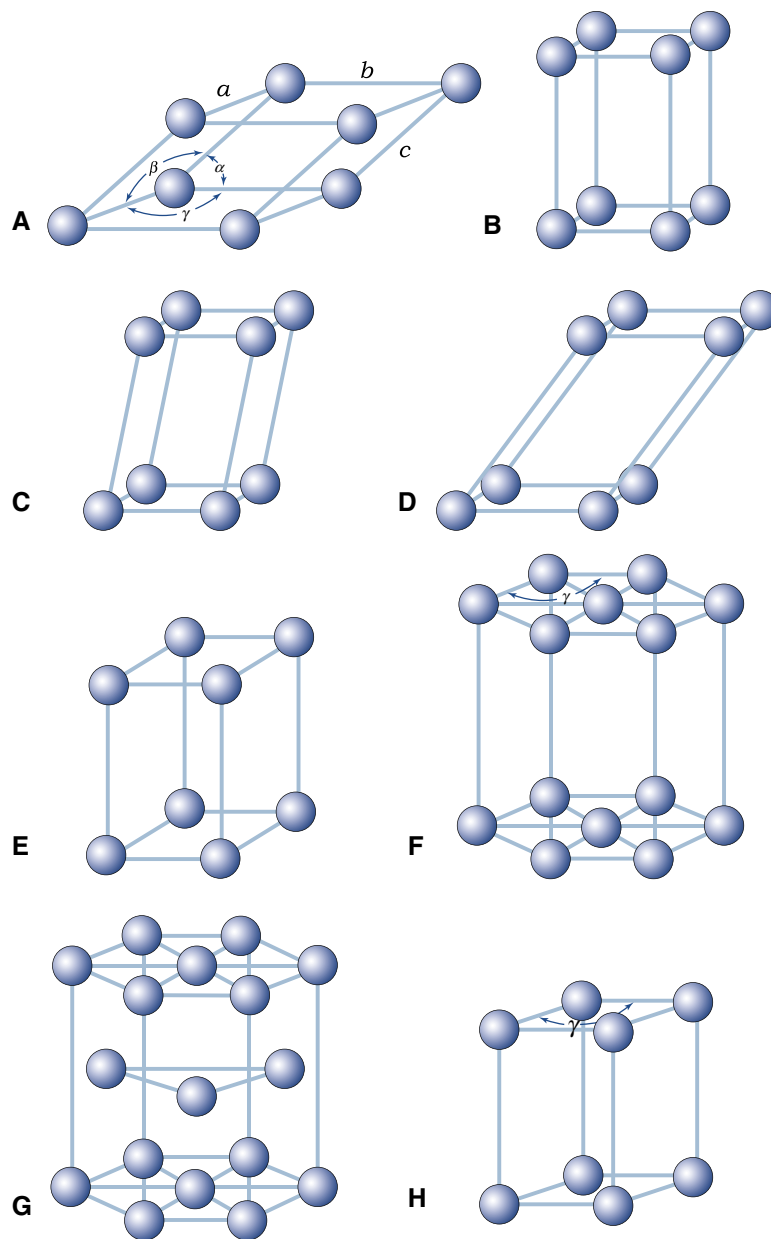
Second, there are a finite number of missing atoms (called *vacancies*) within a solid formed during solidification. A noncrystalline structure, because of short-range order, also contributes some space. Both conditions represent pathways through which diffusion can occur. Atoms change position in pure, single-element solids even under equilibrium conditions; this process is known as *self-diffusion*. As with any diffusion process, the atoms or molecules diffuse in the solid state to reach an equilibrium state. Just as ink disperses uniformly in water, a concentration of atoms in a solid metal can also be redistributed through the diffusion process.

Diffusion may also occur in the other direction to produce a concentration of atoms in a solid. For example, if the sugar in water becomes supersaturated, the molecules of sugar diffuse toward each other, and the sugar crystallizes out of solution. In the same manner, a solid copper-silver alloy, to be discussed in Phase Diagram, with a higher copper concentration may cause supersaturation of copper in silver, which forces the diffusion of copper atoms to increase the concentration of copper locally, causing them to precipitate.

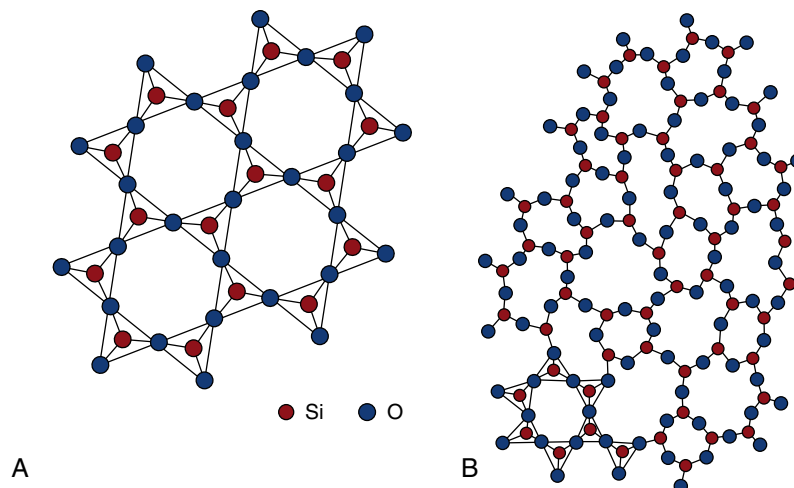
CRITICAL QUESTION

Why are mercury and gallium of interest as components of direct restorative materials?

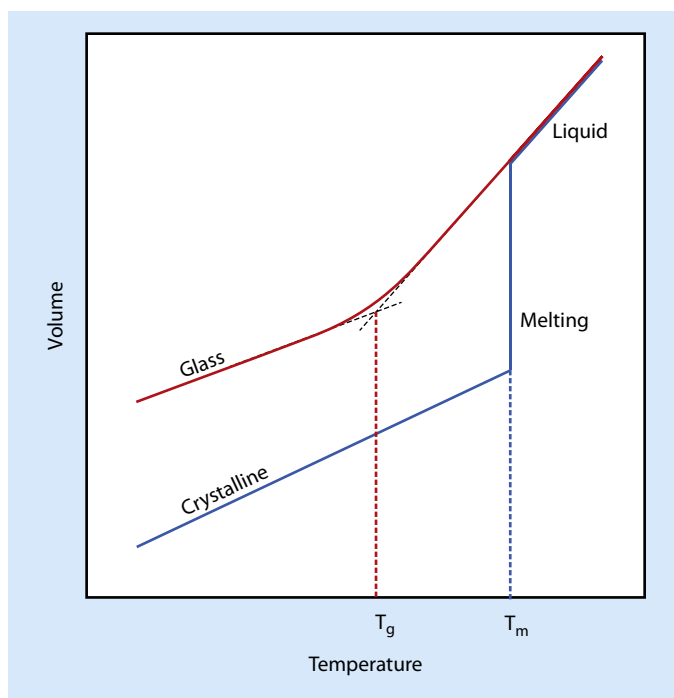
The diffusion of elements in most crystalline solids at room temperature is very low. Yet at temperatures that are a few hundred degrees higher, the bond energy between atoms decreases, thus allowing rapid atomic diffusion. For the same reason, the



• **Figure 2-9** Other lattice types of dental interest. A, Rhombohedral. B, Orthorhombic. C, Monoclinic. D, Triclinic. E, Tetragonal. F, Simple hexagonal. G, Close-packed hexagonal. H, Rhombic.



• **Figure 2-10** Two-dimensional illustration of crystalline (*left*) and noncrystalline (*right*) forms of SiO_2 .



• **Figure 2-11** Plot of glass-transition temperature. The glass-transition temperature (T_g) differs from the melting temperature (T_m), where a crystalline solid changes to a liquid state with an increase of volume. T_g marks the temperature at which major segments of polymer chains begin to gain some translational freedom, as observed by a gradual increase of volume.

diffusion in a crystalline solid of a lower melting point, the rate of diffusion is greater. Diffusion in a noncrystalline material may occur at a more rapid rate and often may be evident at room or body temperature. The disordered structure enables the molecules or atoms to diffuse more rapidly with less activation energy. Both mercury and gallium are liquid at room temperature because of their melting points at -38.36°C (-7.05°F) and 29.78°C (85.60°F), respectively. When either liquid metal is mixed with a suitable metal alloy, atoms in the alloy dissolve and diffuse rapidly within the liquid metal at intraoral temperature. The result is a new solid metal compound. This process has been used in dentistry for making metallic direct restorative materials ([Chapter 8, Amalgam Alloy](#)).

CRITICAL QUESTION

Can you describe metals by their appearance and usage?

Metals

Metals, by their appearance and usage, have several characteristics. A clean, polished metallic surface exhibits a luster that cannot be duplicated by other classes of solids. Most metals emit a metallic sound (“ring”) when they are struck by another metal. They are generally excellent thermal and electrical conductors. Metals are more resistant to deformation or rupture from external forces and denser than nonmetallic structures. Most metals are also far more ductile and malleable than nonmetals, which are generally brittle. The significance of strength, ductility, malleability, and brittleness will be discussed in the chapter on mechanical properties ([Chapter 4](#)). Only

a few metals are resistant to tarnish and corrosion in the air at room temperature.

Pure metals, in common with other elements, can be identified by their specific melting and boiling points and by their basic physical and chemical properties. Some relevant properties for metals of dental interest are listed in [Table 2-1](#). Information about the atom size, crystal structure, and chemical properties of these elements is provided in [Table 2-2](#). Note that several important elements have more than one crystal structure (polymorphic forms), depending on the temperature, and have multiple valences.

Of the 118 elements currently listed in the periodic table ([Figure 2-12](#)), about 88 can be classified as metals. One common feature in the atomic structure of metal elements is that the outermost electrons (valence electrons) around the neutral metallic atoms are easily given up. This property constitutes the basis of the metallic bond, where a “cloud” of valence electrons becomes the “glue” for the positively charged ionic cores made of the nuclei and the balance of the bound electrons. The bond is nondirectional, allowing the ionic cores to break interatomic bonds with facility and establish new bonds with other ionic cores at different positions. This property enables metals to undergo distortion before fracturing (properties of ductility and malleability) under mechanical **stresses**. It should be noted that many metals of importance for dental alloys are transition elements that have incomplete inner electron shells.

CRITICAL QUESTION

Why are pure metals not often used for dental applications?

Pure metals have limited uses in dental and engineering applications because they are too soft to resist deformation from external forces. It has been found that mixtures of two or more metallic elements or mixtures of one or more metals and nonmetallic elements often result in improved properties beyond what the individual elements can provide. This combination of elements is called an **alloy**. An **alloy system** refers to all possible combinations (weight percentage or atomic percentage) of elements in the system. Alloys are generally prepared by fusion of the elements above their melting points. In this book, the term “metal” is used all-inclusively to include alloys and pure metals. If the phenomenon discussed does not apply to both alloys and pure metals, a distinction will be made. The mechanisms for property improvement, and the effects on physical and chemical properties of alloys, will be discussed in some detail in [Chapter 9](#).

To make a metal prosthesis, an exact wax or plastic pattern of the prosthesis is prepared initially. Using a dental investment, an expanded mold is prepared from the pattern, into which the molten alloy is filled under pressure ([Chapter 14, Investing Procedure](#)). When the alloy solidifies, it shrinks to the intended dimensions. The mechanical properties of the final cast prosthesis can often be manipulated by regulating the cooling procedure. In this chapter segment, we will first discuss how a solid emerges from the molten (liquid) state and the resultant microstructure of pure metals. We then will discuss the criteria for forming different types of alloys, the interpretation of phase diagrams, and refinement of the properties of alloys by controlled heating and cooling.

CRITICAL QUESTION

Why do dental alloys begin freezing by heterogeneous nucleation rather than by homogeneous nucleation?

TABLE 2-1 Physical Properties of Elements in Dental Alloys

Element	Symbol	Atomic Weight	Melting Point (°C)	Density (g/cm ³)	Thermal Expansion Coefficient (10 ⁻⁶ /K)
Aluminum	Al	26.98	660	2.70	23.6
Carbon	C	12.01	630	2.22	6.0
Chromium	Cr	52.00	271	7.19	6.2
Cobalt	Co	58.93	1495	8.85	13.8
Copper	Cu	63.54	1083	8.96	16.5
Gold	Au	196.97	1063	19.32	14.2
Indium	In	114.82	156	7.31	33.0
Iridium	Ir	192.20	2454	22.50	6.8
Iron	Fe	55.85	1527	7.87	12.3
Magnesium	Mg	24.31	650	1.74	25.2
Mercury	Hg	200.59	-39	13.55	40.0
Molybdenum	Mo	95.94	2619	10.22	4.9
Nickel	Ni	58.71	1453	8.90	13.3
Palladium	Pd	106.40	1552	12.02	11.8
Platinum	Pt	195.09	1769	21.45	8.9
Rhodium	Rh	102.91	1966	12.44	8.3
Silicon	Si	28.09	1410	2.33	7.3
Silver	Ag	107.87	961	10.49	19.7
Tin	Sn	118.69	232	7.30	23.0
Titanium	Ti	47.90	1668	4.51	8.5
Tungsten	W	183.85	3410	19.30	4.6
Zinc	Zn	65.37	420	7.133	0.4

Data from Lyman T, editor: *Metals Handbook*, vol 1, ed 8, Cleveland, OH, 1964, American Society for Metals.

Solidification and Microstructure of Metals

If a pure metal is melted and cooled to room temperature under very clean laboratory conditions, a graph of its temperature-versus-time behavior would look similar to that in [Figure 2-13](#). The temperature decreases steadily from point A to point B'. An increase in temperature then occurs from point B' to point B, at which time the temperature remains constant until the time indicated at point C is reached. Subsequently, the temperature of the metal decreases steadily to room temperature (point D). The temperature, T_f , indicated by the "plateau" portion of the curve at point BC, is the solidification temperature of the pure metal. This is also the melting point or fusion temperature.

During the initial cooling, the molten metal remains in the liquid state to point B', which is below the solidification temperature; this process is termed *supercooling* or *undercooling*. During the supercooling stage, crystallization of the pure metal begins. Once the crystals begin to form, the release of latent heat from liquid changing to solid causes the temperature to rise to T_f , where it remains until crystallization is completed at point C. Supercooling of pure metals occurs only in clean, inert containers under

circumstances in which *heterogeneous nucleation* of metal crystals is not possible.

Nucleus Formation

Solidification of a metal requires nuclei of crystallization. The liquid state can be imagined as one of a multitude of random atoms surrounding numerous unstable atomic aggregates or clusters that are attempting to form crystal nuclei. These temporary nuclei are called *embryos*. On approaching the solidification temperature, these embryos increase in number and size, but they are still unstable and tend to dissolve into the liquid matrix. However, once the supercooled process is completed, there is a tendency for some of these embryos to survive and thus become solidification nuclei. This method of nucleus formation is called *homogeneous nucleation*, and the formation of nuclei in the molten metal is a random process with equal probability of occurring at any point in the melt.

Another method of forming stable embryos is for the atoms in the molten metal to contact some surface, particles in the melt, or particles in the container. Such a process is known as *heterogeneous*

TABLE 2-2 Atom Size, Crystal Structure, and Chemical Properties of Elements in Dental Alloys

Element	Symbol	Atom Radius (nm)	Crystal Structure	Oxidation States	Electronegativity
Aluminum	Al	0.118	Face-centered cubic	+3	1.61
Carbon	C	0.067	Hexagonal (graphite) Diamond cubic (diamond)	+4	2.55
Chromium	Cr	0.166	Body-centered cubic	+2, +3	1.66
Cobalt	Co	0.152	Hexagonal close-packed ($\leq 450^\circ\text{C}$) Face-centered cubic ($> 450^\circ\text{C}$)	+2	1.88
Copper	Cu	0.145	Face-centered cubic	+1, +2	1.9
Gallium	Ga	0.136	Orthorhombic	+3	1.81
Gold	Au	0.174	Face-centered cubic	+1, +3	2.54
Iron	Fe	0.156	Body-centered cubic ($\leq 911^\circ\text{C}$) Face-centered cubic ($> 911^\circ\text{C}$)	+2, +3	1.83
Mercury	Hg	0.171	(Liquid above -39°C)	+2	2
Molybdenum	Mo	0.190	Body-centered cubic	+6	2.16
Nickel	Ni	0.149	Face-centered cubic	+2, +3	1.91
Platinum	Pt	0.177	Face-centered cubic	+2, +4	2.28
Palladium	Pd	0.169	Face-centered cubic	+2, +4	2.2
Silver	Ag	0.165	Face-centered cubic	+1	1.93
Tin	Sn	0.145	Body-centered tetragonal	+4	1.96
Titanium	Ti	0.176	Hexagonal close-packed ($\leq 880^\circ\text{C}$) Body-centered cubic ($> 880^\circ\text{C}$)	+2, +3, +4	1.54
Zinc	Zn	0.142	Hexagonal close-packed	+2	1.65

Values for atom radius and electronegativity were obtained from <http://periodictable.com/>.

nucleation because a foreign body “seeded” the nucleus. The distribution of these foreign bodies is not necessarily random. Under dental casting conditions, heterogeneous nucleation occurs at the mold wall (investment) or in the molten alloy at impurity particles or particles of special grain-refining elements.

It should be noted that supercooling is not necessary for heterogeneous nucleation. In fact, heterogeneous nucleation should account for most of the nucleation that occurs during dental casting. The uniformity of distribution of heterogeneously formed nuclei is difficult, in principle, to control because the distribution of the different types of “seeds” is not likely to be uniform.

CRITICAL QUESTION

Why might the rates of cooling and solidification affect the grain size of a dental casting?

Liquid-to-Solid Transformation of Cast Metals

As a liquid metal cools and solidifies, crystals are formed by diffusion of atoms from the molten metal to existing nuclei of crystallization. The crystals extend along certain favored crystallographic directions and form dendrites. The heat released by the solidifying metal (in extending the arms of dendrites) reduces supercooling around the arm, which impedes solidification in affected regions and results in highly elongated extension of the arms. Subsequently, secondary

extension arms of the dendrites branch off the primary arms, and tertiary arms off the secondary arms, resulting in a three-dimensional dendritic structure. Dendrites can also grow perpendicular to the walls of the mold cavity toward the center of the casting. Numerous dendritic crystals form and grow until they eventually become large enough to impinge upon each other. Solidification is completed when the liquid metal in the interdendritic spaces between the dendrite arms freezes to yield crystals. Each crystal within the solidified metal is called a **grain**. Thus a grain is a microscopic single crystal that has a different orientation from that of the adjacent grains. The interface between adjacent grains is called a **grain boundary**. The solidified metal is also called *polycrystalline*.

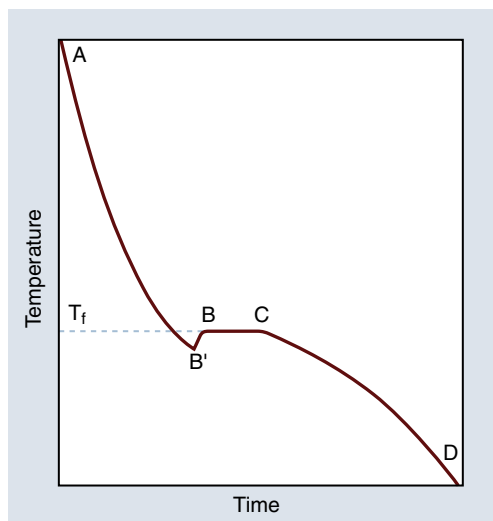
The grain boundaries in a solidified metal are revealed when examining the **microstructure** of a polished surface that has been etched. When a highly polished metal surface is subjected to a chemical or an electrolytic etching solution, the atoms near grain boundaries are preferentially removed, creating microscopic grooves that scatter light because these atoms have higher energy compared with atoms in the interiors of grains. An as-cast dendritic pattern may be present, like the Pd-based alloy shown in **Figure 2-14**, or a dendritic microstructure may not exist, such as for the high-palladium alloy having an equiaxed grain structure shown in **Figure 2-15**. The term *equiaxed* means that the three dimensions of each grain are similar, in contrast to the elongated shape and size of the dendrites in **Figure 2-14**.

Periodic Table

Periodic table																						
1 IA																18 VIIIA						
1	1 Hydrogen H																	2 Helium He				
2 IIA																13 IIIA 14 IVA 15 VA 16 VIA 17 VIIA						
2	3 Lithium Li	4 Beryllium Be															5 Boron B	6 Carbon C	7 Nitrogen N	8 Oxygen O	9 Fluorine F	10 Neon N
3	11 Sodium Na	12 Magnesium Mg															13 Aluminum Al	14 Silicon Si	15 Phosphorus P	16 Sulfur S	17 Chlorine Cl	18 Argon Ar
3 IIB 4 IVB 5 VB 6 VIB 7 VIIB 8 VIIIB 9 VIIIB 10 VIIIB 11 IB 12 IIB																						
4	19 Potassium K	20 Calcium Ca	21 Scandium Sc	22 Titanium Ti	23 Vanadium V	24 Chromium Cr	25 Manganese Mn	26 Iron Fe	27 Cobalt Co	28 Nickel Ni	29 Copper Cu	30 Zinc Zn	31 Gallium Ga	32 Germanium Ge	33 Arsenic As	34 Selenium Se	35 Bromine Br	36 Krypton Kr				
5	37 Rubidium Rb	38 Strontium Sr	39 Yttrium Y	40 Zirconium Zr	41 Niobium Nb	42 Molybdenum Mo	43 Technetium Tc	44 Ruthenium Ru	45 Rhodium Rh	46 Palladium Pd	47 Silver Ag	48 Cadmium Cd	49 Indium In	50 Tin Sn	51 Antimony Sb	52 Tellurium Te	53 Iodine I	54 Xenon Xe				
6	55 Cesium Cs	56 Barium Ba	57-71 Series of Lanthanide Elements	72 Hafnium Hf	73 Tantalum Ta	74 Tungsten W	75 Rhenium Re	76 Osmium Os	77 Iridium Ir	78 Platinum Pt	79 Gold Au	80 Mercury Hg	81 Thallium Tl	82 Lead Pb	83 Bismuth Bi	84 Polonium Po	85 Astatine At	86 Radon Rn				
7	87 Francium Fr	88 Radium Ra	89-103 Series of Actinide Elements	104 Rutherfordium Rf	105 Dubnium Db	106 Seaborgium Sg	107 Bohrium Bh	108 Hassium Hs	109 Meitnerium Mt	110 Darmstadtium Ds	111 Roentgenium Rg	112 Copernicium Cn	113 Nihonium Nh	114 Flerovium Fl	115 Moscovium Mc	116 Livermorium Lv	117 Tennesse Ts	118 Oganesson Og				

Series of Lanthanide Elements	57 Lanthanum La	58 Cerium Ce	59 Praseodymium Pr	60 Neodymium Nd	61 Promethium Pm	62 Samarium Sm	63 Europium Eu	64 Gadolinium Gd	65 Terbium Tb	66 Dysprosium Dy	67 Holmium Ho	68 Erbium Er	69 Thulium Tm	70 Ytterbium Yb	71 Lutetium Lu
Series of Actinide Elements	89 Actinium Ac	90 Thorium Th	91 Protactinium Pa	92 Uranium U	93 Neptunium Np	94 Plutonium Pu	95 Americium Am	96 Curium Cm	97 Berkelium Bk	98 Californium Cf	99 Einsteinium Es	100 Fermium Fm	101 Mendelevium Md	102 Nobelium No	103 Lawrencium Lr

• **Figure 2-12** Periodic chart of the elements.



• **Figure 2-13** A time-temperature cooling curve for a pure metal, illustrating supercooling.

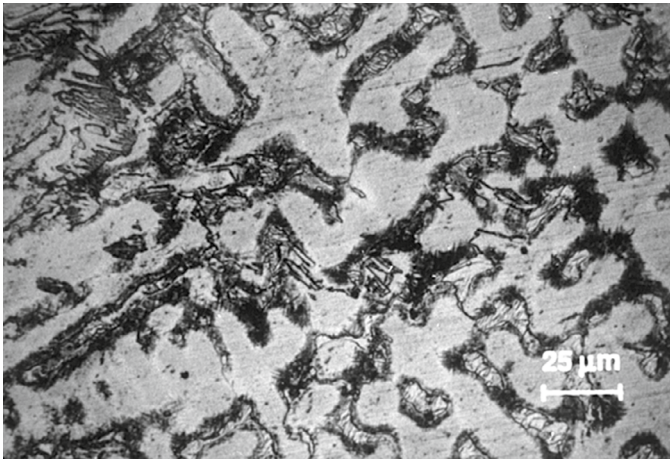
Figure 2-16 is a schematic illustration of the coalescence of individual grains to form an equiaxed grain structure. Solidification starts from isolated nuclei in the molten metal, and these crystals gradually grow by the clustering of atoms and extend toward each other. When the adjacent crystals are eventually in contact, their growth stops, as shown in Figure 2-16, E. The final polished and etched microstructure depicting grain boundaries is shown in Figure 2-16, F. The grain boundary regions are the last portions of the molten metal to solidify and can serve as sites for precipitate formation and sinks for impurity atoms.

CRITICAL QUESTION

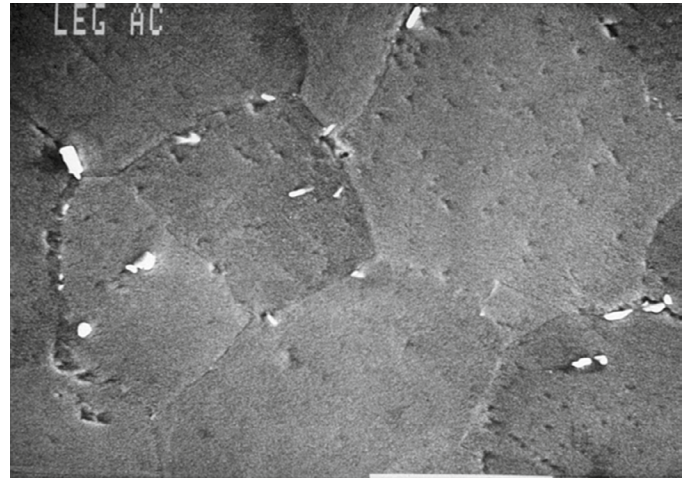
How does the grain size affect the properties of cast dental alloys?

Grain Refinement and Grain Size

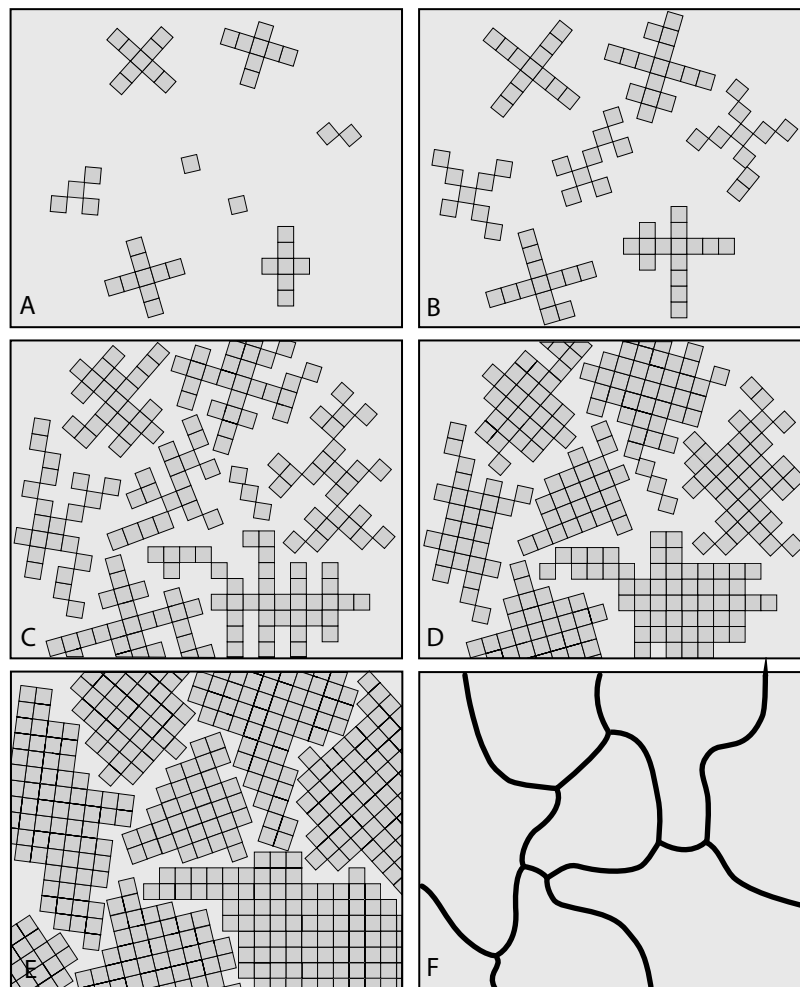
In general, the smaller the grain size of the metal, the better are its physical properties. For example, the yield strength of many metals has been found to vary inversely with the square root of the grain size. Consequently, obtaining a small grain size during casting is an advantage.



• **Figure 2-14** Optical microscopic image of a polished and etched palladium-based alloy with a dendritic as-cast microstructure. Higher-magnification scanning electron microscope (SEM) images reveal that the complex interdendritic regions can contain a eutectic constituent. (From Carr AB, Brantley WA: New high-palladium casting alloys: part 1. Overview and initial studies. *Int J Prosthodont* 4:265, 1991. Reproduced with permission from Quintessence Publishing Company, Inc.)



• **Figure 2-15** Scanning electron microscope (SEM) image of a polished and etched high-palladium alloy with an equiaxed fine-grain as-cast microstructure. The white-appearing particles are ruthenium-rich and arise from the use of ruthenium as a grain-refining element. (From Brantley WA, Cai Z, Foreman DW, et al: X-ray diffraction studies of as-cast high-palladium alloys. *Dent Mater* 11:154, 1995. Reproduced with permission.)



• **Figure 2-16** Stages in the formation of metallic grains during the solidification of a molten metal. (Redrawn from Rosenbain W: *Physical metallurgy*, ed 2, London, 1928, Contable and Co.)

There are two variables that can reduce the grain size during solidification: number of nuclei of crystallization and rate of crystallization. A greater number of nuclei will yield a greater number of grains, and thus the size of each grain is reduced. As pointed out previously, the formation of nuclei of crystallization can be increased by the amount of supercooling and the rate of cooling. If the crystals grow more rapidly than the formation of nuclei of crystallization, the grains will be larger than if the reverse condition prevails. Conversely, if the formation of nuclei occurs faster than the growth of crystals, a small grain size will be obtained. Consequently, slow cooling results in large grains. In other words, the more rapidly the liquid state can be changed to the solid state, the smaller or finer the grains will be. Small concentrations of high-melting-point metals, such as iridium (Ir), ruthenium (Ru), or rhenium (Re), are generally added as grain-refining elements to noble metal casting alloys for dental prostheses.

CRITICAL QUESTION

Why should a dentist or lab technician consider both the weight percentage and the atomic percentage of potentially toxic elements when selecting an alloy for dental prostheses?

Solid Solutions

We often associate a solution with a liquid; therefore the term **solid solution** would appear counterintuitive. In chemistry, a *solution* refers to a type of homogeneous mixture composed of two or more substances. That means we could have a solution in the solid, liquid, or vapor state. The key word is *homogeneous*. Consider the palladium-silver (Pd-Ag) alloy system, which is relevant for an important group of metal-ceramic alloys ([Chapter 9, Palladium-Silver Alloys](#)), as an example. When an alloy in this system is solidified, the silver atoms are distributed randomly in the space lattice of the palladium atoms, thereby forming a solid solution. Because the silver atoms become integrated into the crystal structure of palladium, no microstructural evidence of a mechanically removable phase exists because there is only one phase. The term **phase** in chemistry is defined as a physically distinctive and homogeneous region of matter. If the binary Pd-Ag alloy appears to be inhomogeneous as a result of improper cooling, it can be heat-treated at elevated temperatures for sufficiently long times to promote solid-state diffusion that ensures the uniform distribution of silver atoms in the palladium lattice.

Solutes and Solvents

In liquid solutions, the substance present in the greater amount is the solvent, and the substance of the lesser amount uniformly dispersed in the solvent is the solute. The same principle applies in solid solutions, where the solute atoms are uniformly dispersed in the crystal structure of the solvent atoms. There are two principal atomic arrangements for solid solutions.

The first type is the *substitutional solid solution*, in which the atoms of the solute occupy the positions in the crystal structure that are normally occupied by the solvent atoms in the pure metal. For a Pd-Ag alloy, the crystal structure of both elements is FCC, and Ag atoms replace Pd atoms randomly in the crystal structure of Pd; Ag is the solute, and Pd is the solvent. The second type is the *interstitial solid solution*, in which the solute metal atoms are present in random positions (interstices) between the atoms in the crystal structure of the solvent metal. This type of solid solution requires that the solute atoms be much smaller in

diameter than the solvent atoms, and these solid solutions are usually limited to relatively small concentrations of solute. The family of carbon steels is an example of an interstitial solid solution of carbon in iron. Another example is commercially pure titanium (CP Ti), an alloy for implants and restorative dentistry ([Chapter 9, Titanium and Titanium Alloys](#)), which consists of high-purity (≥ 99 wt%) titanium, with oxygen, carbon, nitrogen, and hydrogen atoms dissolved interstitially.

Conditions for Solid Solubility

According to the four Hume–Rothery rules discussed in textbooks on engineering materials science, the conditions that dictate solubility of metals for forming substitutional solid solutions are as follows:

1. Type of crystal structure—The crystal structure of the solute and the solvent metals should be identical.
2. Atom size difference—The atomic radii of the solute and solvent atoms must differ no more than 15%; otherwise, multiple phases occur during solidification.
3. Valence—Solid solutions are more likely to occur when the solvent and solute atoms have the same valence.
4. Electronegativity—Electronegativity is an atom's tendency to attract a bonding pair of electrons. Alloys with a greater difference in electronegativity between the solute and solvent atoms tend to form intermetallic compounds rather than solid solutions. *Intermetallic compound* refers to a substance composed of definite proportions of two or more elemental metals, like AuCu and AuCu₃ in the Au-Cu alloy system to be discussed later.

According to [Table 2-2](#), the difference between the atomic diameters for Ag and Sn is approximately 4%. However, these two metals differ in valence and have different crystal structures, so there is limited solid solubility for Sn in Ag. As the Sn content increases, an intermetallic compound (Ag₃Sn) forms, which is an important phase in the starting powder for preparing dental amalgams ([Chapter 8, Amalgamation](#)).

For an interstitial solid solution, the solute metal atoms must be smaller than the size of the interstitial spaces in the solvent metal lattice, and the solute and solvent atoms must have similar electronegativity to avoid the formation of intermetallic compounds.

Mechanical Properties of Solid Solutions

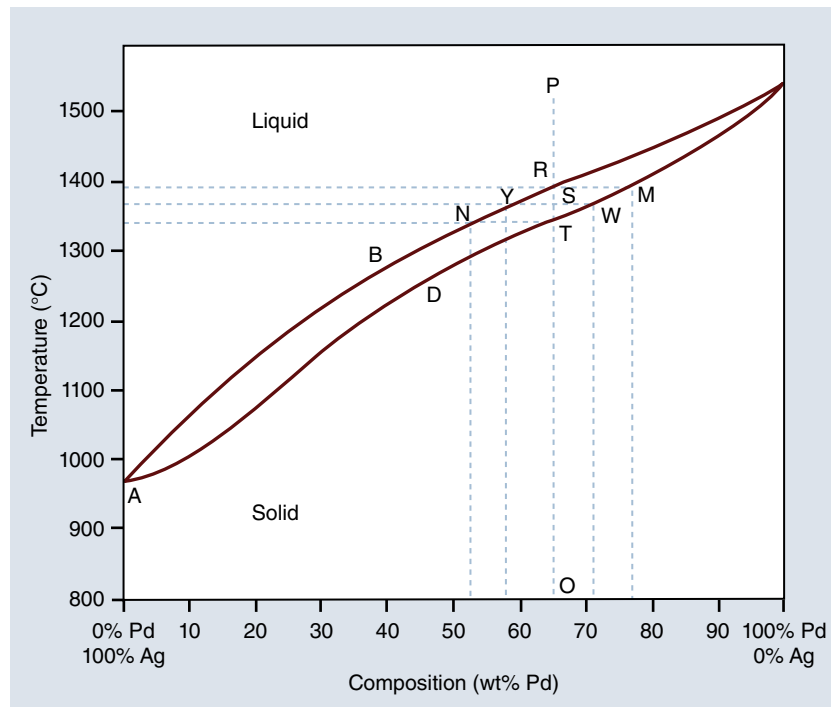
Substituting solute atoms of different sizes in the solvent lattice causes localized distortion, which is known to improve the mechanical properties of alloys, such as greater force or pressure needed to cause deformation of the material. For example, although pure gold in the cast condition is too soft for restorations, adding only 5 wt% of copper will provide adequate strength and hardness to the Au-Cu alloy that are sufficient for the casting to be used for small inlays. Mechanisms of strengthening metals through alloying will be discussed later in this chapter and in [Chapter 9, Dislocation Movement in Polycrystalline Alloys](#).

CRITICAL QUESTION

Why is the study of binary phase diagrams important, even though dental alloys contain more than three elements and the conditions during solidification and cooling after casting are far removed from equilibrium?

Equilibrium-Phase Diagrams

A **phase diagram** shows conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases occur



• **Figure 2-17** Equilibrium-phase diagram for the palladium-silver system showing percentages by weight. Only the percentage composition for palladium is given; the percentage composition for silver is determined by subtracting the palladium composition from 100.

and coexist at equilibrium. The phase diagrams in this book are temperature–composition graphs showing the boundaries of phase transformation in two-element alloy systems under atmospheric pressure. For three-component alloy systems, a three-dimensional (3-D) phase diagram is needed to include the third element but would be much more complex. (Two-dimensional portrayals of important ternary phase diagrams for three-component alloy systems are provided in engineering reference texts.) Nevertheless, binary phase diagrams are useful for understanding the structure of alloys. **Figure 2-17** presents the phase diagram for the solid solution Pd-Ag system. These two elements exhibit complete solubility in both liquid and solid states. Note the liquid, liquid-plus-solid (L + S), and solid regions separated by the liquidus (upper) and solidus (lower) curves. The *liquidus* is the boundary between the liquid and (L + S) regions, and the *solidus* is the boundary between the (L + S) and solid regions.

Interpretation of a Solid-Solution Phase Diagram

The dashed line PO in **Figure 2-17** represents cooling of a liquid metal containing 65% Pd and 35% Ag from 1500 °C (point P) to 800 °C (point O). At approximately 1400 °C, line PO intersects the liquidus at point R, where solidification begins. We can draw a parallel line through point R that intersects the solidus at point M. The line RM is called a *tie line*. The meaning of the tie line is that the initial solid phase that forms at that temperature should have the composition of point M, 77% Pd, when projected to the horizontal (composition) axis; the composition of the liquid remains essentially the same because only a very small amount of solid has precipitated.

When the temperature decreases to point S (~1370 °C), the new compositions of the solid and liquid phase may be determined by the tie line YW, a parallel line drawn through point S intersecting the liquidus at point Y and the solidus at point W.

Projecting points Y and W to the horizontal axis shows that the solid formed is 71% Pd and the remaining liquid phase is 57% Pd. When the vertical cooling line intersects with the solidus at point T (~1340 °C), the tie line NT shows that if there is any liquid left at this temperature, the remaining liquid should have the composition of 52% Pd (point N). Most if not all of the liquid has converted to solid with 65% Pd (point T). When the temperature decreases below point T, the alloy is entirely solid, with a composition of 65% palladium.

It should be reemphasized that the phase diagram describes the equilibrium state of the alloy for the different compositions–temperature conditions. The cooling process would have to be held at each of the foregoing temperatures for a prolonged time sufficient for atomic diffusion to enable the approach to equilibrium conditions for both the liquid and solid phases.

CRITICAL QUESTION

Why does solidification of metal alloys from fluid state always yield a solid with inhomogeneous microstructure?

Coring and Homogenization Heat Treatment

In practice, cooling of a casting does not allow phases in the alloy to reach equilibrium at each temperature before solidification is completed. For example, the first stable nucleus that forms at the temperature point R (or slightly below) in **Figure 2-17** is richer than 65% Pd. As the solidification continues with temperature decreasing, the Pd content in the liquid decreases so that each succeeding “layer” that solidifies on this nucleus will have reduced Pd content and increased Ag content than the previous layer. Before reaching the solidus temperature (point T) in **Figure 2-17**, the composition (point N) of the remaining liquid to solidify between the outermost layers of the adjacent solid particles would have

Ag richer than 35%. The solid particles (dendrites or grains) have what is termed a *cored structure*, with the composition varying from the center (containing more Pd) to the outer surface (containing less Pd). Thus the central portion of each particle contains larger amounts of the component with the higher solidification temperature (Pd), and the outer portions contain larger amounts of the component with the lower solidification temperature (Ag). It follows, because more atomic diffusion would be required to achieve near-equilibrium compositions, that the larger the temperature range between liquidus and solidus, the greater is the tendency toward coring.

A cored structure represents an inhomogeneous microstructure, making alloys more prone to tarnish and corrosion (Chapter 3, *Heterogeneous Surface Composition*). For Pd-Ag alloys, it is necessary to have Pd dispersed uniformly for providing tarnish and corrosion resistance in the oral environment (which causes silver to tarnish). Alloys with heterogeneous microstructures have greater resistance to permanent deformation than alloys with homogeneous microstructures, as discussed in Chapter 9, *Dislocation Movement in Polycrystalline Alloys*. The ductility of an alloy that is single phase under equilibrium conditions increases after a homogenization heat treatment that eliminates nonequilibrium secondary phases.

CRITICAL QUESTIONS

What are the advantages and disadvantages of eutectic alloys? How do the alloy compositions of binary eutectic systems affect their properties?

Eutectic Alloys

When the two metals in a binary system have the same crystal structure but limited mutual solid solubility, the phase diagram may include two solid solutions, one rich in the first metal and one rich in the second metal. Figure 2-18 shows a phase diagram for the Ag-Cu system and a schematic microstructure of each phase. Three phases can be observed: a liquid phase (L), a silver-rich substitutional solid-solution phase (α) containing a small percentage of copper atoms, and a copper-rich substitutional solid-solution

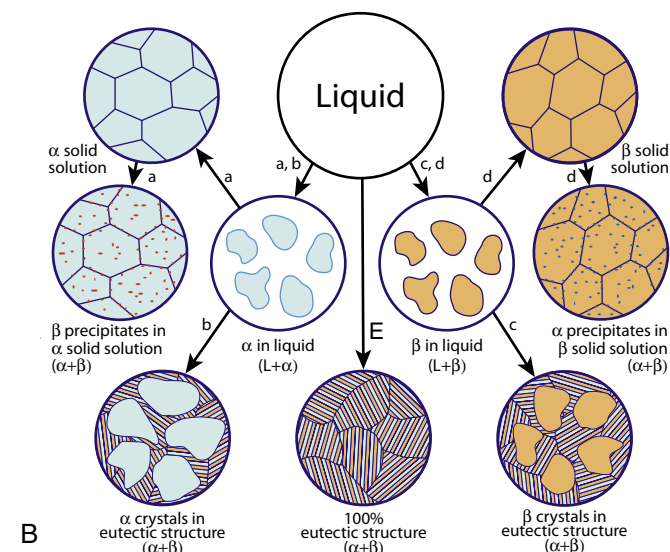
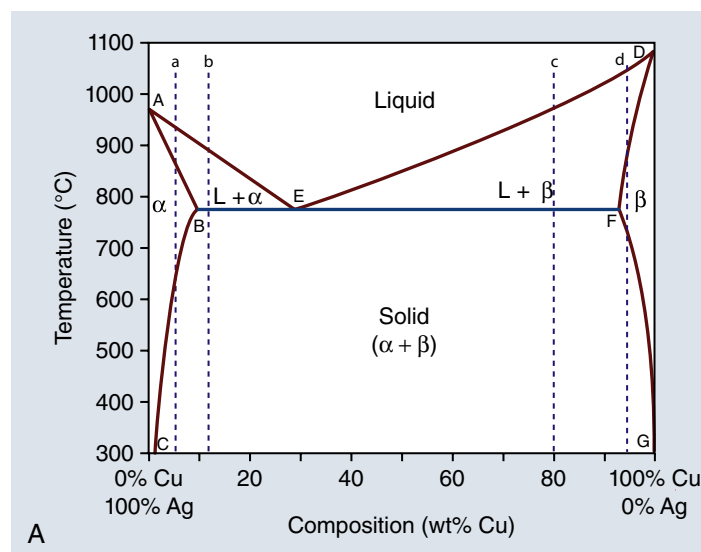
phase (β) containing a small percentage of silver atoms. The solidus curve is the boundary line ABEFD, and the liquidus curve is AED. In the $\alpha + \beta$ region (CBEFG), both solid solutions exist. Note that the alloy composition represented by point E has the lowest melting point of the alloy system. The composition of point E is known as the *eutectic composition*, 28% Cu and 72% Ag, for the Ag-Cu alloy system. Because point E is also on the solidus curve, the eutectic composition should solidify completely at a single temperature (the eutectic temperature) that is referred to as an *invariant point*.

Phase Changes of Eutectic Alloys

The Ag-Cu phase diagram (Figure 2-18, A) represents a typical binary eutectic phase diagram and is used in the following discussion of the phase changes that can occur during cooling. Line ABC (termed a *solvus line*) shows the solid solubility of Cu in silver for the α solid solution as the temperature changes; this solid solubility reaches a maximum at point B (~9% at 780 °C). Solvus line DFG shows that the solid solubility of Ag in Cu reaches a maximum at point F (~8% at 780 °C) but has a very low value at 300 °C (point G).

The eutectic liquid composition solidifies at a single temperature to a solid phase comprising two phases (α and β). A lamellar structure with alternating layers of the α and β phases typically forms, such as shown in Figure 2-18, B, because a minimal amount of diffusion is required to produce the needed segregation of the two different atom species.

Figure 2-18, B illustrates phase-transformation equilibrium cooling of five different alloy compositions in the Ag-Cu system. For the molten 5% Cu alloy (line a), cooling to the (L + α) region causes precipitation of α crystals within the liquid. Further cooling past line AB results in complete solidification of the alloy to α solid solution. As the alloy is cooled further, the solubility limit at line BC forces precipitation of β solid solution within α , typically at grain boundaries or interdendritic regions. There is no eutectic microstructure for this alloy composition because the cooling (vertical dashed line) does not cross the eutectic isotherm line (line BEF). When the cooling of a liquid-phase (line b) alloy containing 12% Cu crosses points AE, crystals of α emerge in the



• **Figure 2-18** Equilibrium-phase diagram of a eutectic alloy. **A**, Silver-copper system showing percentages by weight. **B**, Diagram of all possible phase transformations in the silver-copper system. Note that the ratio of phases is not to the scale of the composition.

liquid. When this alloy cools past line BEF, the remaining liquid forms a lamellar eutectic structure around existing α crystals. The amount of the eutectic constituent in the microstructure of the solid alloy depends on how close the alloy composition is to the eutectic composition. For the alloy containing 80% Cu (line c), the changes in composition during cooling are similar as in line b, except that now the first solid to form as crystals in the liquid phase is the β solid solution. At a temperature below points BEF, this alloy will have β crystals surrounded by the lamellar eutectic structure. For the molten 94% Cu alloy (line d), the sequence of phase transformation is the same as in line a, except that it forms β solid solution instead.

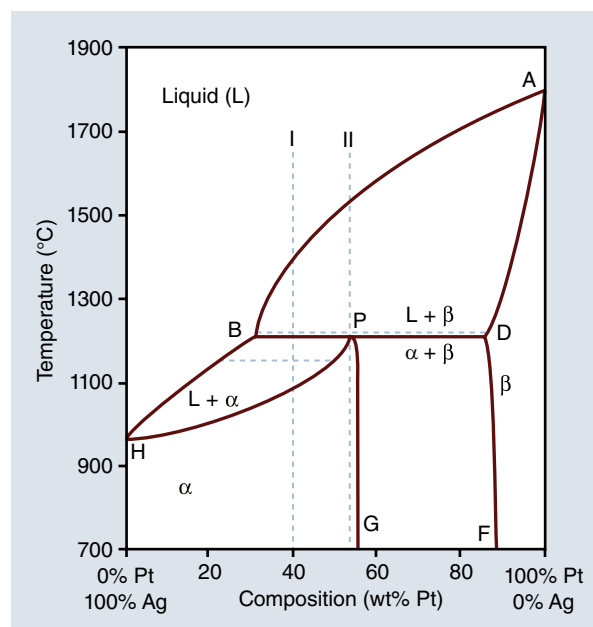
Physical Properties and Application of Eutectic Alloys

Alloys that contain the eutectic constituent in their microstructures are relatively brittle, whereas alloys with microstructures lacking the eutectic constituent are ductile. Alloy embrittlement occurs because the alternating lamellae of the α and β phases inhibit the movement of dislocations, which increases strength and hardness but decreases ductility. The tarnish resistance of these alloys without the eutectic constituent is superior to that of the alloys containing this constituent.

Eutectic alloys have several important applications in dentistry because they correspond to a composition with the lowest melting point in an alloy system. They can be used as filler metals in the processes of brazing or soldering (Chapter 9, Joining of Dental Alloys). The Ag-Cu eutectic composition is also used to produce spherical particles that are combined with Ag_3Sn lathe-cut particles to be reacted with mercury to form a dispersed-phase dental amalgam (Chapter 8, Composition).

Peritectic Alloys

Like the eutectic transformation, the peritectic reaction is an invariant reaction that occurs at a particular composition and temperature. Figure 2-19 is the phase diagram for the Ag-Pt alloy system, which is useful for instructional purposes, although there is no Ag-Pt dental alloy. The pure metals Ag and Pt have the FCC structure. Rather than the difference in atomic radii, the dominant factor is the considerably greater difference in melting temperature for Ag and Pt compared with Ag and Cu. The α phase in the Ag-Pt system is silver-rich, the β phase is platinum-rich, and the two-phase ($\alpha + \beta$) region results from the limited solid solubility of less than approximately 12% Ag in Pt at 700 °C (point F). Figure 2-19 also shows that the equilibrium solid solubility of Pt in Ag is approximately 56% at 700 °C (point G). The peritectic transformation occurs at point P (alloy II), where the liquid (composition at point B) and the platinum-rich β phase (composition at point D) transform into the platinum-rich α phase (composition at point P). For a composition, such as exists for alloy I, cooling through the peritectic temperature results in the transformation of the liquid and β phase ($L + \beta$) to the α phase, with some of the liquid phase remaining ($L + \alpha$). For both of these transformations, the α phase forms at the interface between the liquid and β phase. Because extensive diffusion is required in these phases for the transformation to occur, peritectic alloys are highly susceptible to coring during rapid cooling. This cored structure has inferior corrosion resistance and is more brittle than the homogeneous solid-solution phase. The peritectic reaction in the Ag-Sn system is of great importance for the alloy that reacts with mercury to form dental amalgam for restorations, as discussed in Chapter 8, The Silver-Tin System.



• **Figure 2-19** Equilibrium-phase diagram of the platinum-silver system showing percentages by weight.

Solid-State Reactions in High-Noble and Noble Alloy Systems

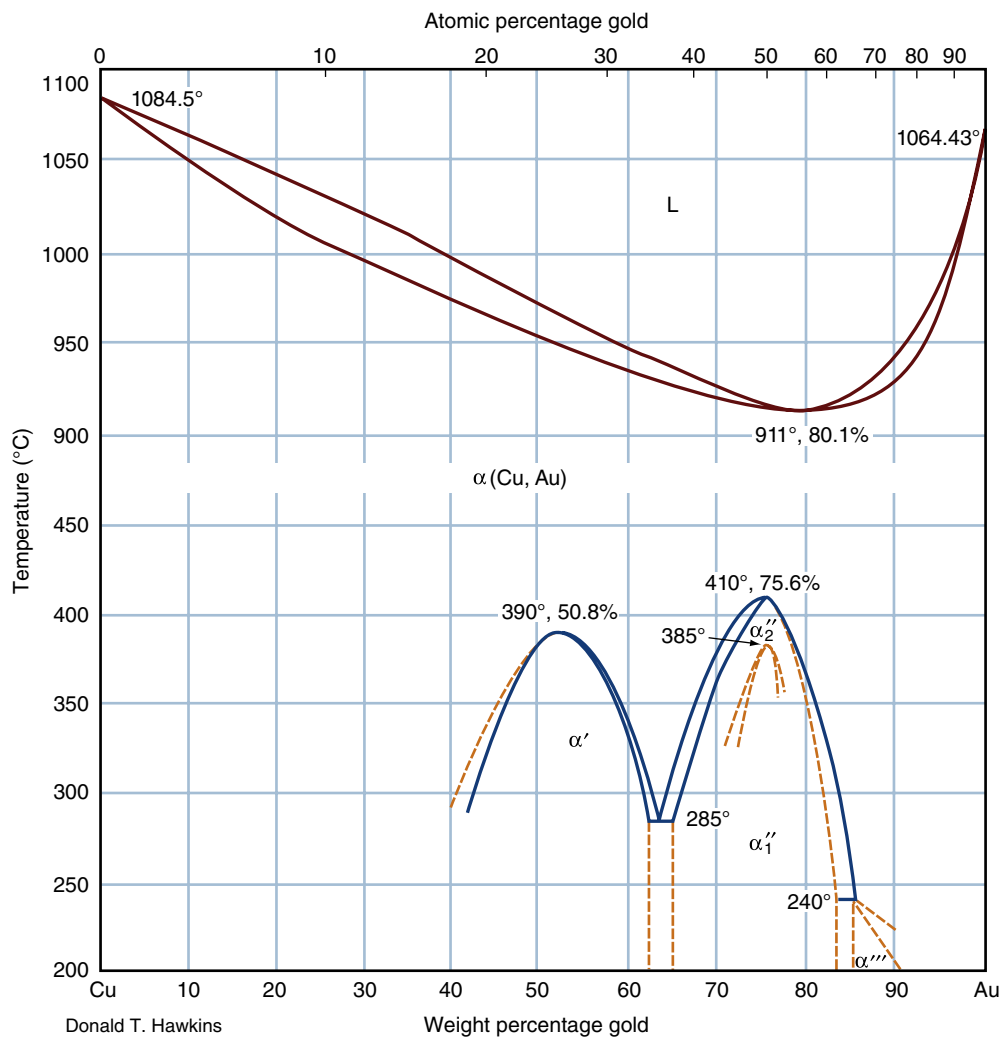
The strength and hardness in some metal alloys may be manipulated by the presence or absence of uniformly dispersed fine particles or certain phases within the original matrix phase. The process can be achieved via a solid-state reaction (i.e., a controlled heating and cooling protocol, also called *heat treatment*) without changing the configuration of the object. The best-known example is the ordering of Au-Cu alloys.

CRITICAL QUESTION

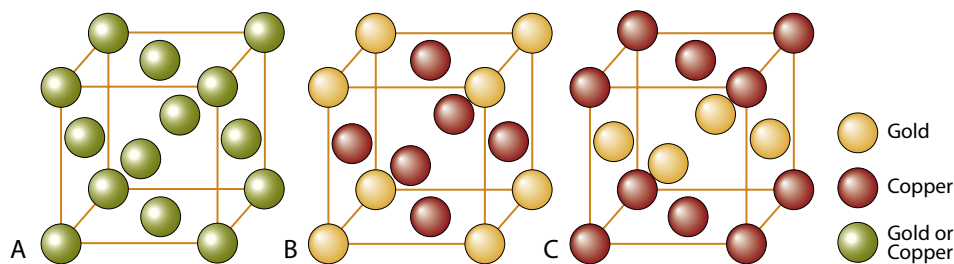
By which two mechanisms does copper provide strengthening and hardening of gold casting alloys?

Gold-Copper System

Figure 2-20 presents the Au-Cu phase diagram, where both weight and atomic percentages are shown. The melting range between the solid and liquid phases is narrow for all compositions, and the liquidus and solidus curves meet at 80.1 wt% Au. At the lower half of the diagram, there are two arch-shaped regions. One arch spans the composition range between 40 and 65 wt% Au and peaks at 390 °C with 50.8 wt% Au (α'). The atomic ratio of Au to Cu at the peak is 1:3, indicating the formation of the intermetallic compound AuCu_3 in this region. The second arch spans the composition range between 65 and 85 wt% Au and peaks at 410 °C with 75.6 wt% Au (α_2''). The atomic ratio of Au to Cu at this peak is 1:1, indicating the formation of intermetallic compound AuCu in this region. The α solid solution that forms when the alloys initially solidify has a disordered structure in which the Au and Cu atoms randomly occupy the lattice sites (Figure 2-21, A). The AuCu and AuCu_3 phases have new crystal structures that differ from the parent FCC α solid solutions of Au and Cu atoms that form when the alloys initially solidify at elevated temperatures below the solidus curve (Figure 2-21, B & C). These phases in the regions under



• **Figure 2-20** Equilibrium-phase diagram for the gold-copper system. (The temperature range between 450 and 900 °C has been condensed.) (With permission from *Metals handbook*, ed 8, vol 8, Metals Park, OH, 1973, American Society for Metals, p 267.)



• **Figure 2-21** Structure of Au-Cu alloy. **A**, Disordered substitutional solid solution. **B**, Superlattice of AuCu_3 . **C**, Superlattice of AuCu .

the two arches are called *ordered* because the Au and Cu atoms occupy specific locations in the lattices.

Because the crystal structure of the ordered phase (termed a *superlattice*) differs from that of the gold α solid solution, each region of the ordered phase is surrounded by a localized elastic **strain** field, which is necessary to maintain the continuity of atomic bonds across the interface between the ordered phase and the matrix α phase. As a result, it requires greater strength to cause plastic deformation of the alloys ([Chapter 9, Dislocation Movement in Polycrystalline Alloys](#)).

Rapid cooling of a molten gold alloy in a room-temperature water bath or an ice-water bath (also known as *quenching*) does not allow sufficient time for atomic diffusion to form the ordered structure. The disordered solid solution is retained at room temperature, and the gold alloy is relatively soft and ductile. Bench cooling of the same gold alloy through the temperature range of ordered phase formation allows enough atomic diffusion for partial transformation to an ordered structure that provides the additional strength. Clinically, a type 3 or 4 gold alloy casting can be quenched after initial solidification to retain a soft disordered structure, which

allows easier adjustment of the casting, such as the margin, and then reheated to a specific temperature within the ordered-phase region (e.g., 400 °C) for a period of time as recommended by the manufacturer and quenched to yield the stronger and harder ordered alloy. This process is called *age-hardening heat treatment*.

To reverse the hardened type 3 or 4 gold alloy castings to their softened condition, the casting is heated to a temperature below the solidus temperature (e.g., 700 °C), holding for approximately 10 minutes to convert the alloy to the disordered substitutional solid solution, and then quenched to retain the disordered phase. The process is called a *solution heat treatment*.

It should be noted that the quenched, softened condition for types 3 and 4 gold alloys is metastable, and slow increases in hardness and strength will occur with time under room-temperature or intraoral conditions as a result of low-temperature ordering.

Other Noble Alloys for Dental Applications

Dental gold casting alloys may contain solute metals (Cu, Pd, and Pt), which provide solid-solution strengthening, along with minor amounts (<1%) of Zn or Ir forming precipitates, leading to age hardening. Because commercial dental alloys contain multiple elements, interactions between solute atom species have the potential to influence microstructures and mechanical properties. Because of elemental microsegregation during rapid solidification and cooling, phases may be observed in cast dental alloys that would not occur under equilibrium conditions for the same alloy compositions. Furthermore, the compositions of phases in multicomponent alloys will generally be more complex than in binary alloys. In principle, under equilibrium conditions, each phase in an alloy will contain some amount (which may be minuscule) of each component element.

It is important to note another effective age-hardening mechanism in gold alloys: formation of the FePt₃ intermetallic compound, which provides strengthening of the original high-gold alloys for metal-ceramic prostheses (Chapter 9, Au-Pt-Pd Alloys).

CRITICAL QUESTION

Why are there substantial differences between the microstructures and strengthening mechanisms for the high-palladium alloys and the palladium-silver alloys?

Palladium-Based Alloys

Palladium-based alloys are very important for ceramic applications (Chapter 9, High Noble and Noble Alloys). The high-palladium alloys are based on the Pd-Ga system, in which there is an eutectic composition at the high-palladium-content side of the phase diagram, and complex precipitation reactions potentially occur at lower temperatures. For Pd-Cu-Ga alloys, both the rapid cooling rate during solidification and the addition of copper shift the Pd-Ga eutectic composition to higher percentages of palladium that result in the formation of a Pd₂Ga eutectic phase in the cast microstructure. Both Pd-Cu-Ga alloys and the Pd-Ga alloys have a fine submicron “tweed” structure that can be observed by transmission electron microscopy. This structure appears to form by a martensitic phase transformation in the FCC structure of the palladium solid-solution matrix and remains stable during the firing cycles for dental porcelain. Strengthening of these alloys occurs by the solid-solution mechanism and by the formation of Pd₅Ga₂ precipitates in some Pd-Cu-Ga alloy compositions. In contrast, the Pd-Ag alloys are based on the binary alloy system discussed earlier in this chapter and have much simpler microstructures than the high-palladium alloys, with secondary

phases forming in the Pd solid-solution matrix because of the solute atoms in the alloy compositions. Heat treatment of these alloys can cause microstructural changes that significantly affect mechanical properties.

Multicomponent Dental Alloy Systems

Various age-hardening mechanisms have been employed (often empirically) by alloy manufacturers, and these may vary depending on the alloy composition. There are many possible ternary alloys, quaternary alloys, and higher-order multicomponent alloy systems that can be used for restorative dentistry. Such systems are complex, and the phase-diagram data available are extremely limited. Thus binary phase diagrams are often used to estimate the effect of individual elements on the phases formed, along with the resulting microstructures of these cast alloys. However, such equilibrium diagrams should be interpreted carefully because actual casting and cooling processes reflect nonequilibrium conditions.

Ceramics

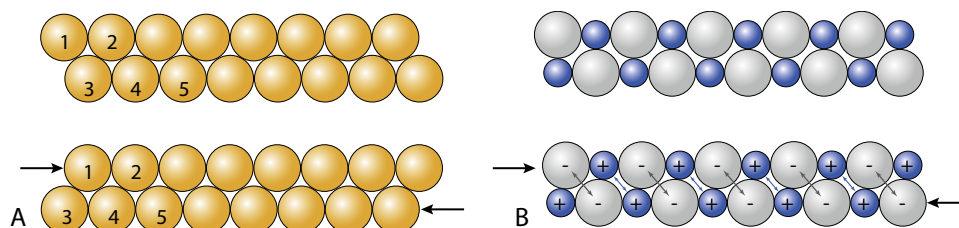
Ceramics are solid-phase compounds of metallic and nonmetallic elements. Recall that the valence electrons of metallic atoms can be transferred to nonmetallic atoms or groups of atoms with outer shells that are nearly complete with electrons to form stable compounds by ionic bonds, and that nonmetallic atoms may also share electrons to form another kind of compound by covalent bonding. Both scenarios deprive compounds of free electrons, thus making them poor conductors of heat and electrical current. Even though they comprise metallic elements but lack characteristics of metal substance, ceramics are considered nonmetallic, inorganic structures.

In the search for the ideal restorative material, dental ceramics have become attractive because of their biocompatibility, long-term color stability, chemical durability, wear resistance, and ability to be formed into precise shapes, although in some cases, ceramics require costly processing equipment and specialized training for lab technicians. In this segment, we will discuss the general structure of ceramics and how the structure affects the mechanical properties of ceramics. Further information on the structure, properties, benefits, and drawbacks of specific ceramic materials used for crown and bridge prostheses will be provided, along with recent developments in dental ceramics.

Structure of Ceramics

Like metals, ceramics have 3-D crystalline structures, but they are much more complicated than those of metals because they need to accommodate different kinds of atoms, maintain electric charge neutrality within the unit cell, and achieve high packing efficiency. Normally, the metallic elements lose their original crystalline structure and adopt a new one. Consider magnesium oxide (MgO), a significant ingredient in investment materials (Chapter 14, Phosphate-Bonded Investment) and modern dental ceramics (Chapter 10, Ceramic-Ceramic or All-Ceramic Systems); Mg in metallic crystal has a hexagonal structure (Figure 2-9, *F*), and the structure of MgO, which is the same as NaCl (Figure 2-7, *B*), shows that anions O²⁻ (large orange spheres) retain an FCC structure, whereas Mg²⁺ ions (small blue spheres) are in the interstitial locations because they are smaller in size. Current dental ceramics are based on silicate ([SiO₄]⁴⁻ tetrahedron), alumina (Al₂O₃), and zirconia (ZrO₂).

Soda-lime glass is a silicate-based material commonly used for windowpanes, glass containers (bottles and jars), and artworks.



• **Figure 2-22** Comparison of slip. **A**, Monoatomic metals of Au. **B**, Biatomic ceramic of MgO; Mg is shown by the blue spheres, and oxygen is shown by the gray spheres. More force is required to displace atoms because of attraction between different atoms and repulsion between similar atoms.

It is manufactured by melting raw materials, which are silica, soda, lime, and a small quantity of varieties of metallic oxides. It has all the ingredients needed to form crystalline structures, but the composition used in soda-lime glass yields short-range, repetitive-order structures. Therefore, ceramic materials with a short-range repetitive order of their structural units are usually called *glasses* or *glassy phase*, which are also transparent to the light. Glassy phases of ceramic melt at lower temperature. They play an important role in the fabrication of ceramic-based prostheses ([Chapter 10, Metal-Ceramic Systems](#)).

The complexity of crystalline and the strong bonds holding the atoms together make the solid-state reactions of ceramic sluggish. At a normal cooling rate, the ceramic does not have enough time to arrange itself into the complicated crystalline structure it could achieve. We, nonetheless, can subject these materials to a heat treatment like that of Au-Cu system by nucleation and growth of crystals in the glass-matrix phase. This type of material is used in dentistry to balance the translucency and opacity of the prostheses. They are called *glass-ceramics* ([Chapter 10, Ceramic-Ceramic or All-Ceramic Systems](#)).

Most metal-forming operations depend on the casting of molten metal and/or mechanical forming of the metal. These operations are rarely used in ceramic-forming operations because of the high melting point and almost extreme brittleness (no ductility) of ceramics. We will learn in [Chapter 10, History of Dental Ceramics](#), that fabricating dental ceramics into prosthetic shapes and configurations is conducted through one of the three categories of processes: sintering, hot isostatic pressing, and computer-aided design/computer-aided manufacturing (CAD-CAM) (see also [Chapter 15, Prototyping Tools](#)). A prosthesis is first sculpted out of dental ceramic powder with the help of a binder, which is followed by a heating process called *sintering*. During sintering, the packed ceramic particles are densified and agglomerate to the intended form. Primary bonding occurs between the particles by liquid-phase sintering with a glassy phase, or solid-state sintering. The preparation of hot isostatic pressing is like metal casting, except that dental ceramic is not melted but softened enough to be pressed into a mold with a cavity of the shape of the prosthesis. CAD-CAM comprises all processes that require the use of a computer to control the making of prostheses. Each of the three structures of the ceramics discussed earlier can be formulated to facilitate each of the three fabrication processes.

Mechanical Properties of Ceramics

Most ceramic materials are described as brittle; that is, they are incapable of large deformations without fracture. Let us examine the deformation of a metal (Au) and a ceramic (MgO) in terms

of atoms' movement between two rows of atoms ([Figure 2-22](#)) in response to a pair of forces pushing the top row right and bottom row left. In the case of metal, every atom in the top row must break a metallic bond with one atom and reconnect with another one in the bottom row. For example, atom 2 breaks a metallic bond with atom 3, and then reconnects with atom 5. The coordination arrangement is the same as before ([Figure 2-22, A](#)). This kind of movement is called *slip*, and the interphase where it occurs is called a *slip plane*. In the case of ceramic, which consists of Mg^{2+} and O^{2-} ions, a similar movement necessitates the breaking of strong ionic bonds, like the gold atoms need to break metallic bonds. Before the ions complete the transition to restore the original atomic arrangements, they must overcome the high-energy positive-positive and negative-negative repulsion forces when they encounter ions of the same charge ([Figure 2-22, B](#)). The entire process requires a tremendous expenditure of energy. This requirement restricts the mechanism of slip in ceramic materials.

Thus slip restriction makes ceramic materials brittle and more resistant to fracture under compression but not under tension. In practice, defects such as pores within the bulk and cracks on the surface are often introduced during processing, production, and handling. These irregularities produce stress concentrations in a material ([Chapter 4, Stress Concentration](#)). For ductile materials, such as gold, the stress concentration can be relieved by atomic slippage. For brittle materials, the stress concentration cannot be relieved and can easily exceed the tensile strength of the materials, causing fracture. Under compression, defects like cracks do not accentuate the stress. Thus, ceramic materials are much stronger in compression than in tension. The role of defects in the longevity of ceramic-based prostheses and means of minimizing the impact of these defects are discussed in [Chapter 10, Minimizing the Effect of Stress Concentrations](#).

Polymers

Polymers are a class of natural or synthetic substances composed of very high-molecular-weight molecules with repeating units, called *macromolecules*. For synthetic polymers, each repeating unit is called *mer* in the polymer and a *monomer* before becoming part of the macromolecule by a chemical reaction called *polymerization*. The main chain of a macromolecule is called the *backbone*. Generally, *resin* is a solid or highly viscous substance of plant or synthetic origin that is typically convertible into polymers. For our purpose, *resins* are compositions of either monomers or macromolecules blended with other components to provide a material, after polymerization, with a useful set of properties.

Synthetic resins polymerize randomly from activated local sites. Thus, depending on the ability of the chains to grow from their local activation sites, the molecular chains that form within

a polymeric material will vary in length, shape, and structure. Although the primary bonds are holding the atoms within a polymer chain, there are secondary bonds and/or hydrogen bonds between polymer chains. In addition, polymer chains often become entangled, adding complexity to the structure. As a result, many physical and mechanical properties are determined largely by intermolecular forces. In this section, we will discuss the nature of polymers, their physical and mechanical properties, and polymerization. Restorative, bonding, and prosthodontic applications of polymers are discussed in Chapters 5, 6, and 11, respectively.

Fundamental Nature of Polymers

Polymerization is a repetitive intermolecular chain-growth reaction that can proceed almost indefinitely, sometimes reaching molecular weights as high as 50 million. The two most significant features of polymers are very large molecules and virtually limitless chain configurations and conformations.

Molecular Weight

Because of the various length of chains in the polymer, a method of expressing an “average” molecular weight of a heterogeneous polymer is needed for the overall molecular weight of polymers. The number average molecular weight (\bar{M}_n) is the total weight of a polymer divided by the overall number of molecules present in the material. The number of molecules can be obtained by measuring the osmotic pressure of the polymer solution. The weight average molecular weight (\bar{M}_w), which can be obtained by light scattering of the same polymer solution, is the sum of molecular weight of polymer chains multiplied their respective weight fraction. The International System (SI) unit for the molecular weight of polymers is the same as that of nonpolymer compounds; it is g/mol and is also known as *Dalton* (Da).

Considering the concepts just discussed, the ratio (\bar{M}_w)/(\bar{M}_n) (called the *polydispersity*) of a polymer is a measure of the range and distribution of chain sizes. Polymers with an equal value of (\bar{M}_w) but different values of polydispersity will exhibit somewhat different properties. For example, polymers of higher polydispersity will begin to melt at a lower temperature and have a larger temperature range of melting.

Chain Branching and Crosslinking

It is possible for a growing polymer chain to branch and lose its linear form (Figure 2-23). Branching is analogous to extra arms growing out of a backbone polymer chain; thus the probability of entangled chains increases. When a monomer has more than one site for growing a chain, it can chemically connect two or

more growing chains (Figure 2-24). Because of the interlinking of many chain backbones, a highly **crosslinked** polymeric material can consist of just a few giant molecules or even a single giant molecule.

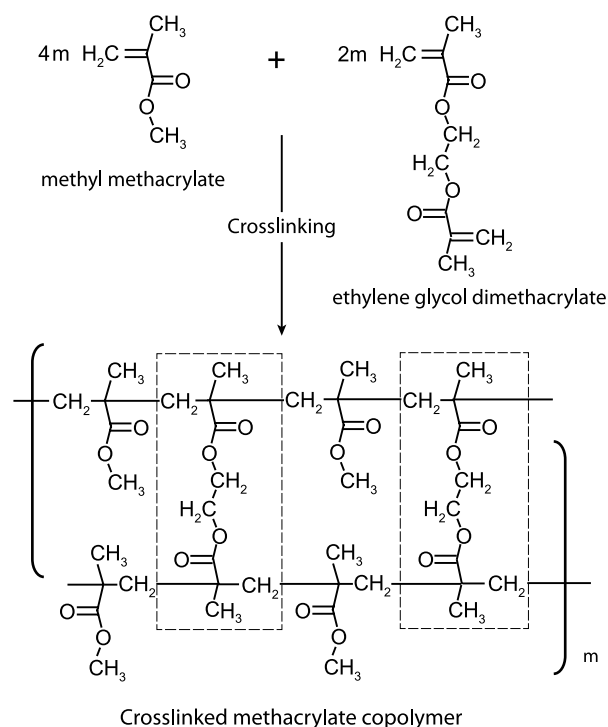
Copolymer Structures

Polymers that have only one type of repeating unit (mer) are homopolymers; those with two or more types of mer units are known as **copolymers**. There are three different types of copolymers by the arrangement of repeating units:

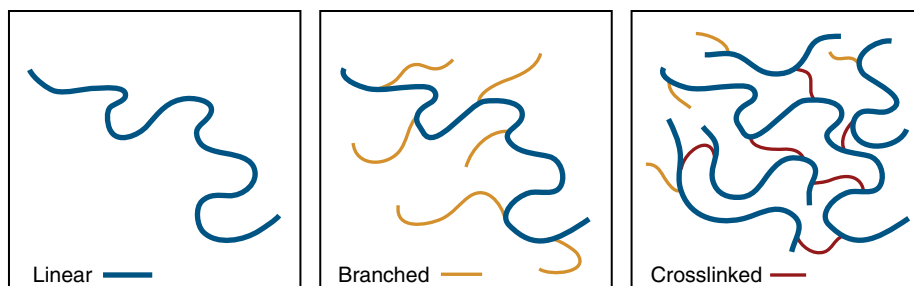
- **Random copolymer**—No sequential order exists among the two or more mer units along the polymer chain.



- **Block copolymer**—Identical monomer units occur in relatively long sequences (blocks) along the main polymer chain.



• **Figure 2-24** A crosslinked structure is formed by copolymerization, where at least one comonomer is multifunctional. Here, methylmethacrylate is copolymerized with ethylene glycol dimethacrylate.



• **Figure 2-23** Schematic diagrams of linear, branched, and crosslinked polymers.

- **Graft or branched copolymer**—Sequences of one type of mer unit (B) are “grafted” onto a backbone chain of a second (A) type of mer unit to form a branched configuration (see Figure 2-23).

```

AAAAAAAAAAAAAAAAAAAAA
  B      B      B
  B      B      B
  B      B      B
  B      B      B
                B
  
```

Molecular Organization

In most polymers, the chains are coiled and entangled in a very random pattern known as an *amorphous structure* (Figure 2-25, left). In others, the chains align themselves to form a highly ordered region, like that of crystalline structures (Figure 2-25, right). Most polymeric materials combine these two forms of organization in greater or lesser proportions. Characteristically, the dental polymers are predominantly amorphous, with little or no crystallinity. The polymer chains form a tangled mass, analogous to cooked spaghetti, in which each spaghetti string is a mile or so long. Such polymer segments have little chance to migrate and are immobile in the solid state.

However, many linear polymers have regions of long-range ordering that produce a degree of crystallinity depending on the secondary bonds that can be formed, the structure of the polymer chain, the degree of ordering, and the molecular weight. Polymer crystallinity usually increases strength, rigidity, hardness, and melting temperature but at the price of reduced ductility—that is, increased brittleness. Factors that reduce or prevent crystallinity and increase amorphous character include the following:

- Copolymer formation, which inhibits polymer chain alignment
- Polymer-chain branching, which also interferes with chain alignment
- Random arrangement of substituent groups, particularly large side groups that keep polymer chains separated.

Physical and Mechanical Properties of Polymers

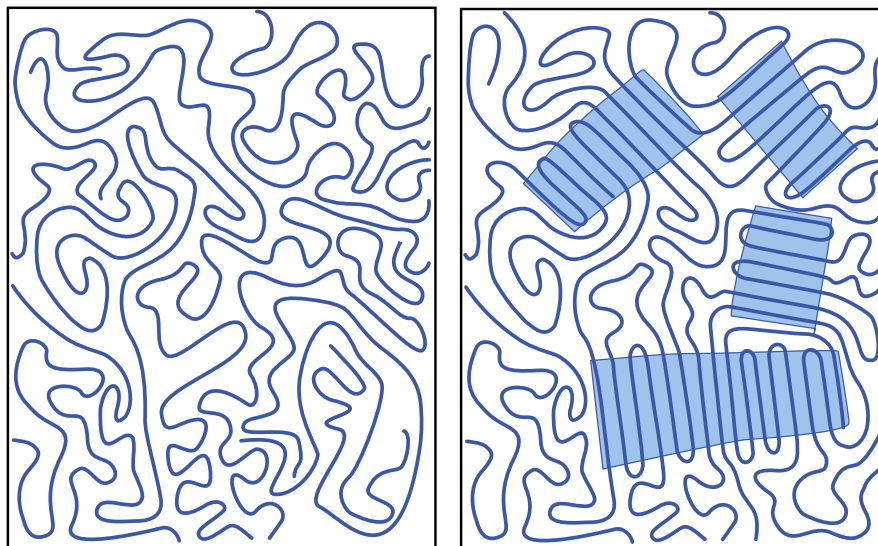
The performance of polymers depends on the interaction between polymer chains and their response to external stimuli. These properties can be grouped into four interrelated categories: mechanical, rheometric, dissolution, and thermal.

Mechanical Properties—Deformation and Recovery

In the absence of crosslinking, only relatively weak interpolymer-chain bonds (van der Waals and hydrogen bonds) are available to hold the polymer chains together in a solid state. Chain slippage decreases as chain length increases because the bonds between chains, together with chain entanglements, resist dislodgment of the individual chains. At a certain chain length, the resistance provided by interchain bonds and entanglements becomes strong enough to exceed the covalent bond strength of the carbon-carbon bonds along the backbone chains. At this critical chain length, an applied force can rupture chains rather than dislodge them and cause one chain to slide past another. This balance between the strength of the interchain bonds and the covalent bonds along the backbone chains explains why the physical and mechanical properties of polymers increase with increased molecular weight up to a certain point. Subsequently, increased molecular weight becomes less important.

Although dependent on its type, a resin generally develops mechanical strength only when its degree of polymerization is relatively high, in the range of approximately 150 to 200 recurring mer units. Above this molecular weight, there is very little increase in strength with further polymerization. Likewise, the molecular-weight distribution of the polymer plays an important role in determining physical properties. In general, a narrow distribution of molecular weight yields the most useful balance among required properties.

Long side chains extending from the main backbone chain (i.e., chain branching) generally produce a weaker resin with a lower softening temperature in comparison with linear-chain (nonbranched) polymers. This weakening occurs because the side chains act to separate the main chains, thus reducing the chain-to-chain attractive forces. This is the *plasticizing* effect discussed further in the following section on solvation. However, if the side



• **Figure 2-25** Schematic diagram of polymers that contain only amorphous intermolecular and intramolecular organization (left) and combinations of both amorphous and crystalline regions (shaded areas on right).

chains can react with adjacent chains to form a crosslinked polymer, the strength of the polymer is increased.

Rheometric Properties

The rheometry, or *flow* behavior, of solid polymers involves a combination of elastic and plastic deformation, followed by **elastic recovery** after the stresses are eliminated. The chain length, number of crosslinks, temperature, and rate of force application (fast impact versus slow extension) determine which type of behavior dominates. A force applied to polymers for an extended period causes the material to undergo all of the following deformations: elastic strain, plastic strain, and viscoelastic strain.

1. **Elastic** strain is reversible deformation and will be quickly and completely recovered when the force is eliminated, as the result of polymer chains uncoiling, and then recoiling (Figure 2-26).
2. **Plastic** strain is irreversible deformation that cannot be recovered and results in a new, permanent shape as a result of slippage among polymer chains (Figure 2-27).
3. **Viscoelastic** strain is a combination of elastic and plastic deformation mentioned in 1 and 2. The elastic portion of the viscoelastic strain will recover when the force is removed, but the recovery takes time to complete because the elastic recovery process is impeded by the viscous flow resistance among chains. The amount of deformation that is not recovered over time is the plastic deformation.

Solvation and Dissolution Properties

When a polymer is immersed in a liquid solvent, it can absorb the solvent, swell, soften, and may even dissolve in the solvent. If the polymer-solvent interactions are higher than the polymer-polymer attraction forces, the polymer chain segment starts to absorb solvent molecules, increase the volume of the polymer matrix, and become solvated in the solvent. It, however, is a slow process. The longer the chains extend, the more slowly the polymer dissolves. Crosslinking provides enough bridges between linear chains to form a 3-D network that decreases solvent sorption, making the polymer nonsoluble. Elastomer, a rubber-like material that is lightly crosslinked, can swell more easily and to a greater extent than do plastics but does not dissolve. Crystalline regions having higher polymer-polymer interaction act as physical crosslinks, reducing swelling and solubility. Chain branching should increase solubility.

The ability to absorb lower-molecular-weight compounds makes it possible to modify the properties of polymers by a process

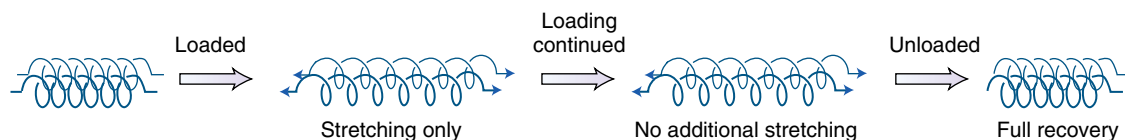
called *plasticization*. Low-molecular-weight compounds, known as *plasticizers*, are often added to resins to lower their softening or melting/fusion temperatures, making a resin that is normally hard and stiff at room temperature, flexible, and soft. For example, polyvinylchloride (PVC) pipe is hard and rigid, whereas PVC water-line tubing is soft and elastic and contains a very high level of plasticizer. In recent years, certain plasticizers, particularly phthalates, have received public attention as a potential ingestion hazard in the soft plastics used in infants' and children's toys.

A plasticizer acts to partially neutralize the secondary bonds or intermolecular attractions that normally prevent the resin chains from slipping past one another (i.e., undergoing plastic flow) when the material is stressed. In some cases, this action is analogous to that of a solvent, with the plasticizing agent penetrating between the chains and increasing the intermolecular spacing. This type of plasticizer is referred to as an *external plasticizer* because it is not a part of the host polymer structure. Its molecular attraction to the host polymer should be high to minimize volatilization or leach-out during the fabrication or subsequent use of the resin.

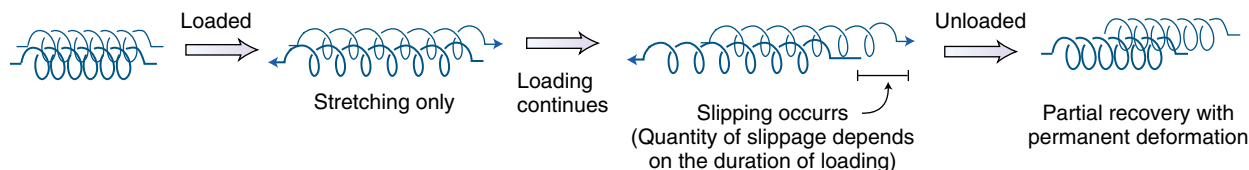
Plasticizing can also be accomplished by copolymerization with a suitable comonomer. In this case, the plasticizing agent becomes part of the polymer and acts as an internal plasticizer. For example, when butyl methacrylate is added to methylmethacrylate before polymerization, the polymerized resin is plasticized internally by the bulky butyl-methacrylate segment. The pendant butyl-methacrylate groups occupy extra space between chains and increase intermolecular spacing, which enhances plastic flow. Plasticizers usually reduce the strength, hardness, and softening temperature of the resin. For example, both types of plasticizers are used to help form soft, cushioning liners for dentures.

Thermal Properties

Polymers can be reshaped into many configurations, depending on whether the polymeric material is a "thermoset" or a "thermoplastic." **Thermoplastic polymers** soften when heated above T_g , the temperature where secondary bonds weaken, and the resin softens and becomes ductile or rubbery (Figure 2-28). Above the T_g , the resin can then be shaped and molded and, upon cooling, retains the new configuration. This process can be repeated almost indefinitely. Thermoplastic resins are made of linear and/or branched chains. Without crosslinking, covalent bonds holding chains together, a polymer can soften (and eventually melt) above T_g and is usually soluble in organic solvents.



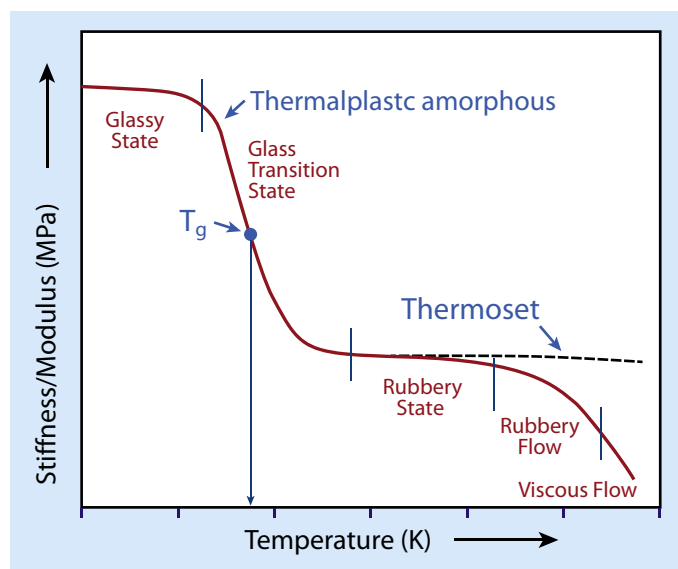
• **Figure 2-26** Elastic recovery: spring-like behavior (rapid and reversible). Chains uncoil, but they do not slip past one another because of crystalline regions, entanglements, or crosslinks. Thus they recoil completely when unloaded.



• **Figure 2-27** Viscoelastic recovery: chains stretch and uncoil and also slip past one another, producing plastic, irreversible, permanent distortion, and partial recovery when unloaded.

In contrast, **thermoset polymers** are formed by heating a precursor mixture, which initiates polymerization, and the ensuing chemical changes render it rigid after cooling. Resins are cross-linked in this state, and thus, they are insoluble and will not melt when heated beyond their glass-transition temperature but instead become rubbery (Figure 2-28). In this manner, the chains are rendered more flexible when heated, and the crosslinks prevent chain slippage and reshaping. Thermoset resins decompose if heated to a high enough temperature.

If two otherwise-similar linear polymers are compared, the one with the higher molecular weight will also have a higher T_g . This is because as the length of the linear-polymer chain is increased, the number of bond sites increases along that chain.



• **Figure 2-28** Effect of temperature on the stiffness of amorphous thermoplastic and thermoset polymers. Both materials exhibit glass-transition and rubbery states. The structure of thermoplastic polymer turns rubbery, and then viscous liquid, whereas thermoset polymer remains rubbery, and then burns. An amorphous polymer takes on characteristic glassy-state properties, such as brittleness, stiffness, and rigidity.

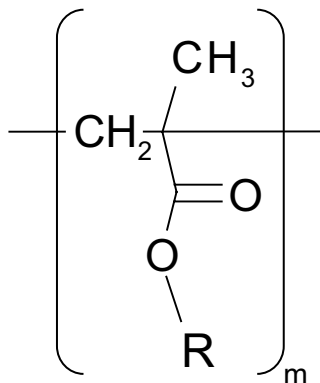
In addition, the longer length of the chain increases the chance for chain entanglements. The number average molecular weight (\bar{M}_n) is indicative of both T_g and the strength of the polymer. As the temperature increases, thermally induced rotations and vibrations among polymer segments increase. This molecular motion forces chains apart, breaks bonds, increases thermal expansion, and facilitates chain disentanglement. These factors, in turn, induce chain slippage and explain the thermoplastic behavior of a resin when the temperature exceeds T_g . As the degree of crosslinking increases, slippage is progressively reduced, and the material becomes progressively more resistant to thermal softening.

Figure 2-29 illustrates the effect of the size and configuration of pendant groups on the T_g of poly(methacrylate) ester compounds. The figure shows that T_g decreases from 125 °C for the shorter methyl group to 33 °C for the longer n-butyl group. The isomer of respective groups, because of compact configuration, results in a smaller reduction of T_g .

Chemistry of Polymerization

Traditionally, there are two classes of polymers as determined by the polymerization mechanism: addition and condensation polymers. Addition polymers contain the same atoms as the monomer in their repeating units, whereas condensation polymers contain fewer atoms because of the formation of by-products during the process. Emphasis, however, has changed to classify polymerization as to whether the process occurs between the functional groups of polymer chains in steps or by propagating of a growing chain by taking in monomers sequentially. Condensation polymers usually are formed by a stepwise intermolecular reaction of reactive functional groups of monomers with multiple functional groups, also known as *step-growth polymerization*. Addition polymers occur by propagation from active growing chains where monomers are sequentially added to one end of the chain, also known as *chain-growth polymerization*. Note that the classification by growth mechanism disregards the existence of by-products; therefore, step-growth polymerization does not always produce by-product, and chain-growth polymerization can yield by-products, depending on the monomers involved.

R		T_g
Methyl	$-\text{CH}_3$	125 °C
Phenyl	$-\text{C}_6\text{H}_5$	120 °C
Ethyl	$-\text{CH}_2-\text{CH}_3$	65 °C
n-Propyl	$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	38 °C
n-Butyl	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	33 °C
iso Propyl	$-\text{CH}(\text{CH}_3)_2$	95 °C
iso-Butyl	$-(\text{CH}_3)_3\text{C}-$	70 °C
sec-Butyl	$-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$	62 °C



Polymethacrylate esters

• **Figure 2-29** Influence of pendant group on the glass-transition temperature of polymethacrylate esters. R represents ester radicals.

CRITICAL QUESTIONS

What are the stages of activation and free radical initiation and curing? Which three activation processes are used for dental polymers?

Addition Polymerization (Chain-Growth Polymerization)

For addition polymerization to occur, monomers must contain an unsaturated bond, which may exist in a double carbon-to-carbon bond or in a ring structure, as shown in Figure 2-30. Carbon-carbon double-bond units are known as *vinyl* groups and are most often exemplified in dentistry by methacrylate monomers ($\text{H}_2\text{C} = \text{CR}-\text{COOCH}_3$). Ring-opening monomers are represented by imine rings found in polyether impression materials (Chapter 13, Polyether) and by epoxy rings found in silorane-based restorative resins (Chapter 5, Low-Shrinkage Monomers).

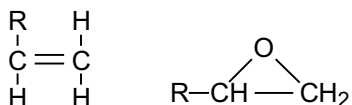
An initiator is also needed to start chain-growth polymerization. The initiator could be a free radical, that is, a substance containing one unpaired electron but that carries no net charge for polymerizing vinyl base monomers ($\text{R}\cdot$), or an ionic compound that carries charges but maintains electrical neutrality as a catalyst for polymerization of monomers comprising rings. Stages of addition polymerization by free radicals are discussed in the following section, using methyl methacrylates, a vinyl monomer, as the model materials. The process occurs rapidly, almost instantaneously, and the reactions are exothermic, with considerable heat evolved.

Stages in Addition Polymerization of Vinyl Monomers

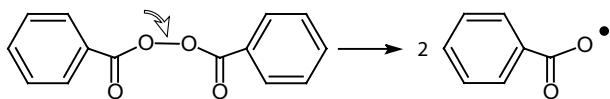
There are four stages in the addition polymerization chain reaction: induction, propagation, termination, and chain transfer.

Induction

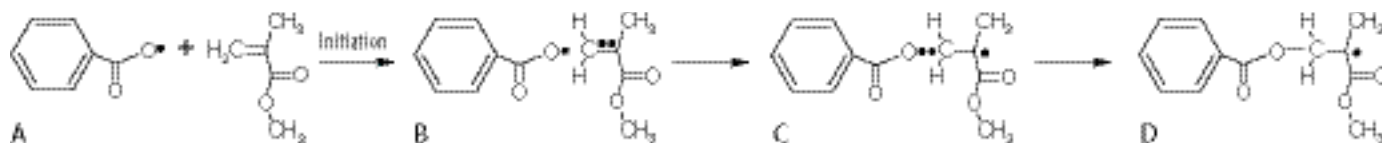
The induction stage comprises two processes: generation of free radicals (activation) and initiation of polymerization. Benzoyl



• **Figure 2-30** Unsaturated functional groups for chain-growth polymerization: vinyl (left) and epoxy ring (right).



• **Figure 2-31** Activation (heat or chemical) of benzoyl peroxide (BPO). During activation, the bond between the two oxygen atoms indicated by the hollow arrow is broken, and the electron pair is split between the two fragments. The dot adjacent to the oxygen atom symbolizes the unpaired electron of the free radical.



• **Figure 2-32** Initiation of a methylmethacrylate molecule by free radical. As the unpaired electron of the free radical approaches the methylmethacrylate molecule (A and B), one of the electrons in the double bond is attracted to the free radical to form an electron pair and a covalent bond between the free radical and the monomer molecule (C and D). When this occurs, the remaining unpaired electron makes the new molecule a free radical (D).

peroxide, which is commonly used in dental resins, can be activated rapidly between 50 and 100 °C or by a second compound, such as amine, to release free radicals (Figure 2-31). The third method is light-activated initiation, which allows control of polymerization with precision by varying light intensity. The latter has become the preferred method of **curing** resin-based composites (Figure 5-5). The stage of curing remains the same regardless of the method of activation. Induction is the period during which initiator molecules become energized and break down into free radicals, followed by these radicals reacting with monomer molecules to initiate chain growth (Figure 2-32). This period is greatly influenced by the purity of the monomer. Any impurities present that are able to react with activated groups can increase the length of this period by consuming the activated initiator molecules. However, the higher the temperature, the more rapid is the formation of free radicals, and consequently, the shorter is the induction period.

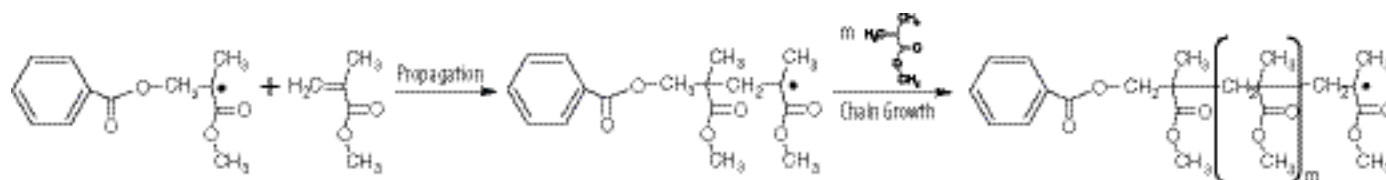
When a free radical approaches a monomer with a high-electron-density double bond, an electron is extracted, and it pairs with the $\text{R}\cdot$ electron to form a bond between the radical and the monomer molecule, leaving the other electron of the double bond unpaired. Thus the original free radical bonds to one side of the monomer molecule and forms a new free radical site at the growing end of the chain (Figure 2-32).

Propagation

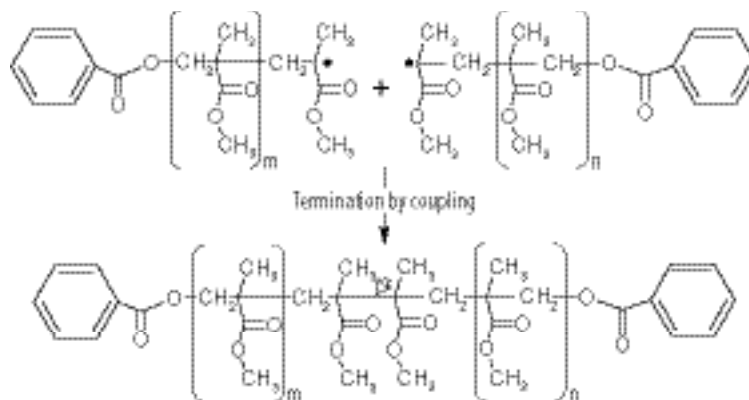
The resulting free radical-monomer complex then acts as a new free radical center when it approaches another monomer to form a dimer, which also becomes a free radical. This reactive species, in turn, can add successively to a large number of methyl-methacrylate molecules so that the polymerization process continues through the propagation of the reactive center. Propagation reactions are further illustrated in Figure 2-33. Because little energy is required once chain growth begins, the process continues with the evolution of heat and leads to large polymer molecules within seconds.

Termination

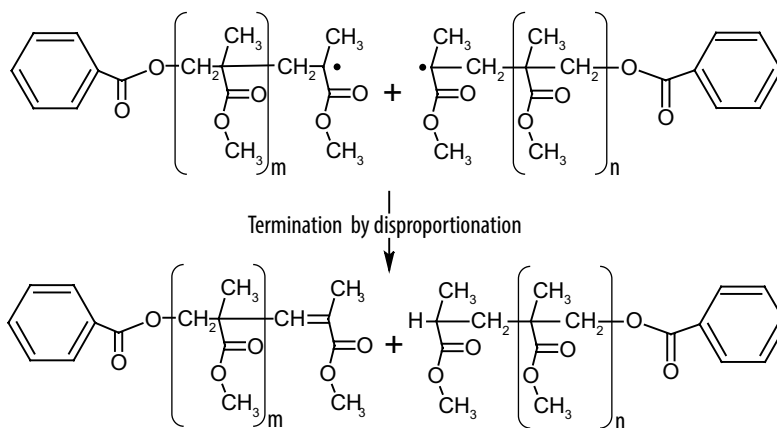
The chain reactions should continue until all the monomer has been converted to polymer chains. However, there is a strong tendency of growing radicals to react and cause termination of chain growth. The probability increases as the monomer concentration decreases. The termination step can occur in two ways: coupling and disproportionation. Coupling is by a direct combination of two free radical chain ends that deactivates the radicals with the formation of a covalent bond (Figure 2-34). Disproportionation involves the transfer of a hydrogen atom from one growing chain to another (Figure 2-35). The free radical donates the hydrogen and becomes unsaturated, while the other one receives the hydrogen and becomes saturated. Therefore there are always unsaturated functional groups remaining in resin-based composite restorations (Chapter 5, Degree of Conversion) and denture bases (Chapter 11, Polymerization Cycle).



• **Figure 2-33** Propagation and chain growth. As the initiated molecule approaches other methylmethacrylate molecules, the free electron interacts with the double bond of the methylmethacrylate molecule and incorporates the molecule to the growing chain, a new, longer free radical is formed.



• **Figure 2-34** Termination occurs when two free radicals interact and are joined together by a covalent bond (*hollow arrow*) but lose their reactivities.



• **Figure 2-35** Disproportionation occurs when two growing free radicals approach each other; one radical becomes an unsaturated end group (*left*) after it donates a hydrogen atom to the other free radical, which becomes a saturated molecule (*right*). The end group that becomes saturated is the passivated segment of the polymer chain.

Chain Transfer

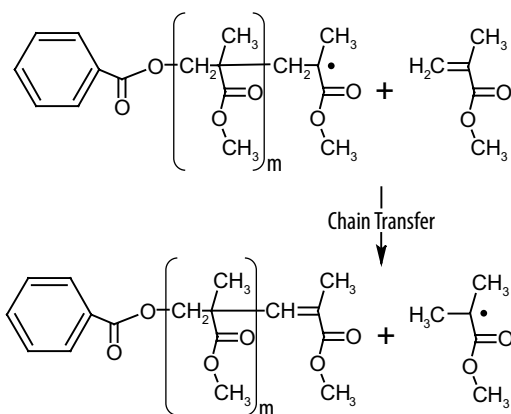
The process of chain transfer involves transferring the reactivity of a radical to another species, along with the termination of the donating radical. The example in [Figure 2-36](#) shows a monomer being activated without the initiator (benzoyl peroxide, BPO). Because the terminated chain gained an unsaturated functional group, it could be reactivated by another chain transfer and continue to grow again.

Inhibition of Addition Polymerization

The polymerization reactions are not likely to result in a complete exhaustion of the monomer, nor do they always form polymers of high molecular weight. Impurities in the monomer often

inhibit such reactions. An impurity can react with the activated initiator or with an activated growing chain and prevent further growth. Although the presence of inhibitors markedly influences the degree of polymerization, the mechanism has been used in resin-based dental materials.

Addition of methyl ether of hydroquinone, a common inhibitor, in the amount of 0.006% or less, inhibits the spontaneous polymerization of dental resins during storage. The inhibitor neutralizes any free radical as it is formed before it initiates chain growth. Therefore all hydroquinone should be eliminated before polymerization by chain propagation can occur. Thus the inhibitor not only prevents premature polymerization during storage but also provides adequate working time in the case of two-part (self-cure) systems.



• **Figure 2-36** Chain transfer occurs when a free radical approaches a methylmethacrylate molecule and donates a hydrogen atom to the methylmethacrylate molecule. This causes the free radical rearrangement to form a double bond and become unreactive, and the methylmethacrylate monomer becomes a free radical without benzoyl peroxide (BPO). The deactivated chain resulting from this exchange can become an active growing chain by a chain transfer from another free radical.

Oxygen reacts readily with the growing chains and results in a radical of low reactivity that does not attract monomers and thus inhibits chain growth. Oxygen inhibition mostly affects the surface exposed to ambient air and produces a greasy film of unpolymerized resin on newly placed sealants and resin-based restorations. The oxygen-inhibited layer generally is unfavorable but can be beneficial in building up a light-cured composite restoration. When new composite is placed over the oxygen-inhibited surface and light-cured, the once-inhibited resin is now shielded from oxygen and exposed to fresh free radicals activated by the light curing. The process promotes bonding between layers of composites. Drawbacks with oxygen inhibition are the higher release of poorly cured material to the adjacent tissues, softer resin (composite) surfaces that are more susceptible to wear and discoloration, and a weaker bond to a tooth surface if the material shrinks away from the oxygen-inhibited layer during curing.

A common clinical practice is to use a matrix material, which helps to shape the resin and acts as a barrier to prevent contact with oxygen during curing. Such a matrix strip prevents a sticky, air-inhibited layer from forming on the surface.

CRITICAL QUESTIONS

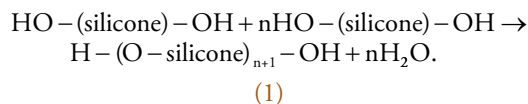
What mechanisms are responsible for the inhibition of polymerization? What are the benefits of inhibitors in dental resins? What role does O_2 play as an inhibitor?

Step-Growth Polymerization (Condensation Polymerization)

The reactions that produce step-growth polymerization can progress by any chemical reaction that joins two or more molecules to produce a simple nonmacromolecular structure. The primary compounds react, often with the formation of by-products such as water, alcohols, halogen acids, and ammonia. The formation of these by-products is the reason step-growth polymerization is often called *condensation polymerization*. This step-growth

mechanism is the one used exclusively in biological tissues to produce proteins, carbohydrates, deoxyribonucleic acid, and ribonucleic acid.

In step-growth polymerization, a linear chain of repeating mer units is obtained by the stepwise intermolecular condensation or the addition of the reactive groups in which bifunctional or trifunctional monomers are all simultaneously active, as opposed to the activation of one monomer at a time of a growing chain in chain-growth addition polymerization. There are two approaches to form condensation polymers: one having both reactive functional groups in one molecule and the other having two types of difunctional monomers. The following example is for the polymerization of one type of diol.



Very often a catalyst is needed to accelerate the reaction, and the resultant molecular weight increases as the duration of the reaction increases. If a monofunctional impurity is present, the reaction will limit the growth of the polymer chain by rendering a chain end inactive.

There are two more examples related to stepwise polymerization in Chapter 13. In one, water is removed in the process of joining one type of monomer (trimercaptan) to form a polysulfide rubber with an oxidizing agent (Figure 13-2); in the other case, ethanol is removed in the process of joining siloxane molecules to form silicone rubber involving two types of monomers (Figure 13-3).

The formation of polymers by step growth is comparatively slow because the reaction proceeds in a stepwise fashion from monomer to dimer to trimer, and so forth, until large polymer molecules containing many mer units are eventually formed. Such a polymerization process tends to stop when the chains have grown to certain sizes that are less mobile and with few functional groups left to react.

CRITICAL QUESTION

What are the practical benefits of using copolymer resins for dental applications?

Copolymerization

Resin-based materials used in dentistry that require polymerization at chairside or in the laboratory usually comprise more than one type of monomer. In many of the polymerization reactions described previously, the macromolecule is formed by the polymerization of a single type of structural unit. However, two or more chemically different monomers, each with some desirable property, can be combined to yield specific physical properties of a polymer. As defined earlier, the polymer formed is a copolymer, and the process of formation is known as *copolymerization*.

Composite Materials

A composite is a material made of two or more constituent components with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. Most importantly, the combination is designed to achieve specific functional properties. The individual components remain separate and distinct within

the finished structure, differentiating composites from mixtures and solid solutions. In modern materials engineering, composites usually consist of one or more discontinuous phases embedded within a continuous phase.

Microstructure of Composite

The discontinuous phase is usually harder and stronger than the continuous phase and is called the *reinforcement* or *reinforcing material*, whereas the continuous phase is named the *matrix* or *binder*. Each class of materials discussed so far can be either the matrix or the reinforcement phase of a composite, or both phases of the composite. The reinforcement phase, which is discontinuous, can be in the form of particles, short fibers in random directions, unidirectional long fibers, woven fabrics, laminates, or honeycomb. The reinforcement phase of the composite materials used in dentistry is mostly glass or ceramic particles and some short fibers. Often the term *filler* is used to represent the reinforcement phase of the particles and short fibers.

Benefit of Composite Structure

The most cited benefits of adding harder, stronger, or tougher fillers to a matrix are the improvement in the stiffness, strength, or toughness of the resulting materials. By the rule of mixtures, the final properties of the material will be between those of the two constituent materials. Strength enhancement alone would not necessarily satisfy the clinician's need at chairside. Clinicians need to prepare materials at chairside, adapt them to the tooth structure, shape them while they are still soft, and then allow the material to set to the hardened stage capable of withstanding the occlusal load (Chapter 1, *Challenges of Dental Materials in the Oral Cavity*). The most noted composite used in modern dentistry is resin-based composite made of a polymeric resin matrix embedded with glass or ceramic particles (Chapter 5, *History of Composites*). The matrix phase alone can be fluid enough to adapt to tooth surfaces and set to a solid. The addition of filler particles to the matrix can increase the viscosity of the mixture, providing the bulk for shaping the matrix phase and rendering much-needed strength. Filler particles, on their own, would have no ability to form a firm solid, but with the help of the matrix phase, fillers can form a useful solid structure. In dentistry, the term *composite* has been used exclusively for resin-based composite materials.

Composite Materials Used in Dentistry

In addition to resin-based composites, the following chapters show that most dental materials, if examined in detail, are composed of dissimilar subunits as in composites. For example, aqueous dental cements are the result of reactive filler particles mixed with an acid solution. The product of reaction becomes a continuous phase, and unreacted particulates are the discontinuous phase (Chapter 7, *History of Dental Cements*). Dental amalgam is the result of the partial dissolution of alloy particles in mercury, where new mercury-rich phases emerge as the matrix holding the unreacted portion of the alloy particles together (Chapter 8, *Amalgamation*). Multiphase metal alloy can have precipitates dispersed in the microstructure. Keep in mind that metal alloys are not treated as composites, but they do possess structures of a composite nature. Dental porcelain consists of a glassy matrix and a ceramic filler particle phase for strengthening purposes (Chapter 10, *Crystalline Particle Strengthening*). Denture-base resins incorporate polymer beads in

the monomer to make the mixture easily workable for processing. Those beads dissolve partially, and the remaining portion is dispersed within the polymerized matrix (Chapter 11, *Acrylic Resins*). Impression materials have a wide range of filler contents facilitating the specific requirements of impression making (Chapter 13, *Chemistry of Elastomeric Impression Materials*). Various allotropic forms of silica (SiO_2) are incorporated in investment material for metal casting to induce fracture resistance at elevated temperatures and provide thermal expansion of the mold during heating to compensate for metal casting shrinkage (Chapter 14, *Investment Materials*). For abrasive instruments, hard abrasive grits use resin (or rubber), metal, and glass (or ceramic) as the binder to make instruments for various surface-reduction and finishing processes (Chapter 16, *Design of Abrasive Instruments*). Not all composite materials mentioned are made with strengthening in mind but, rather, to fulfill other goals, such as the ability to manipulate the material. Nonetheless, adjusting the filler phase to improve the strength of the final material has been done in some of those materials.

Factors Influencing Properties of Composites

The properties of particle-filled resin composites are influenced by three major factors: component properties, filler content by volume, and interfacial interaction between filler and matrix. The matrix phase is characterized by the stiffness and the fillers by particle size, size distribution, specific surface area, and particle shape. The strength of the composite increases with the filler-volume fraction, up to a limit. Both factors are discussed in Chapter 5, *Composition and Function*. Interfacial interaction can considerably affect properties. For the filler in the resin composite to be effective, a good bonding between the filler and the matrix is essential to enable the matrix to transfer the load to the filler to resist fracture. This means that the filler becomes an integral part of the matrix phase.

Recall from the section on types of bonds that both primary and secondary bonds hold materials together. These bonds occur within the same material; for example, metallic bonds form within metals after melting of metal components and solidification. Ceramic powders are packed together and sintered into a solid object. Solid polymer blends can be made by melting two thermoplastics together and solidifying. How do the fillers bond to the matrix? In dental amalgam, there is a chemical reaction between the mercury and metal alloys, where the bonding between filler and matrix is likely the primary bond. It is the same with the aqueous-based dental cements.

For the other materials, the matrix is usually a resinous fluid phase before solidifying, and there is often no chemical reaction between the two components. There must be some sort of interaction between the liquid and the solid keeping them together after the liquid phase solidifies. In the next section, the interactions between the solid surface and the liquid phase in holding these materials together are examined.

Adhesion and Bonding

So far, we have been exploring the attraction between atoms and molecules in the formulation of metals, ceramics, polymers, and composites. It is the formulation of composites that tests our understanding of bonding. Although we do not expect to observe a similar attraction between two nonmagnetized solid objects, we do notice that two solids can adhere to each other with or without the help of a third substance or device. As examples, an artificial denture stays attached to the soft tissue when saliva is present, plaque adherence to

tooth structure facilitates the formation of calculus, and a transmucosal abutment is fixed to the implant root by a screw (Figure 2-37). The first two examples involve bonding at the molecular scale, and the last one, the implant root, is first retained by mechanical means, followed by osseointegration (Chapter 12, *Implant Attachment Mechanism*). Some dental materials are bonded to the hard tissue to replace the missing part of the tooth structure and restore its functions. Therefore an understanding of the fundamental principles associated with bonding is important to the dentist.

When the molecules of one substrate adhere or are attracted to molecules of the other substrate, the force of attraction is called **adhesion** when unlike molecules are attracted, and it is called **cohesion** when the molecules involved are of the same kind. The material that is used to cause adhesion or bonding is known as the **adhesive**, and the material to which the adhesive is applied is called the **adherend**. In a broad sense, bonding is simply a

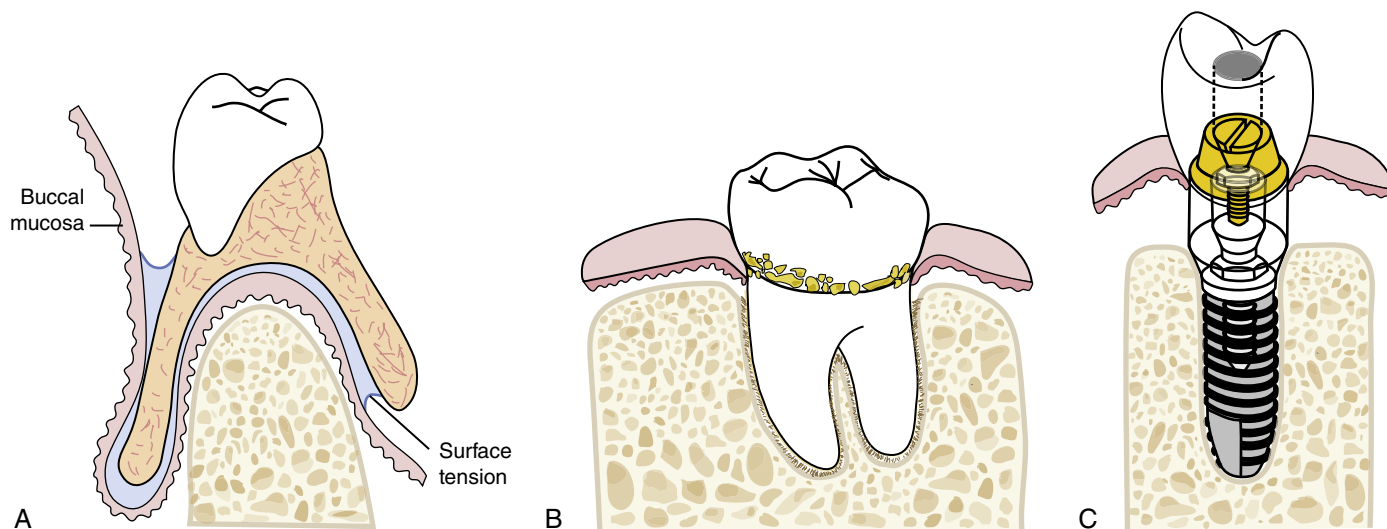
surface-attachment process, which is usually qualified by specifying the type of intermolecular attraction that may exist between the adhesive and the adherend. The application of these concepts is discussed in Chapter 6, *Mechanisms of Adhesion*.

CRITICAL QUESTION

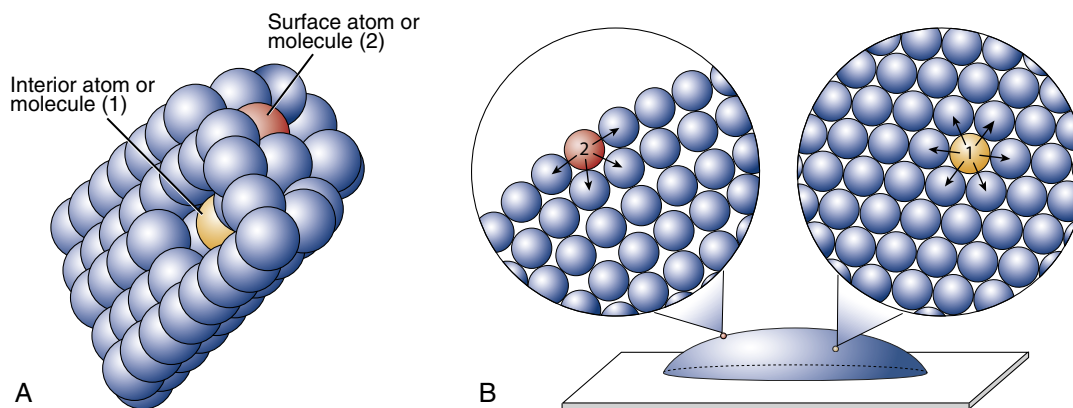
Why is the potential energy of the atoms on the surface higher than those within the bulk of the material?

Surface, Surface Energy, and Surface Tension

A *surface* is defined as the outermost atomic or molecular layer of a material. Consider the space lattice of a solid shown in Figure 2-38, *A*. Inside the lattice, all the atoms are equally attracted to each other. The interatomic attraction for interior atom “1” has a balanced



• **Figure 2-37** Examples of solid adhering to solid in dentistry. **A**, Retention of denture base; saliva fills in the space between the denture and soft tissue, providing retention through capillary attraction (Figure 2-38). The space between the denture and the soft tissue is exaggerated to show the capillary attraction. **B**, Plaque formation on the enamel surface, which converts to calculus by calcification. **C**, The implant root is first retained by the bone mechanically, followed by osseointegration for long-term implant stability. (Courtesy Dr. Inchan Ko.)



• **Figure 2-38** Comparison of atom (or molecule) under the surface with atom (or molecule) on the surface. Each sphere represents an atom or a molecule. **A**, As a solid, a bond balance exists around the interior atom (1), and the exposed atom (2) on the surface is free to develop bonds to atoms or molecules approaching the surface. **B**, As a liquid, the interior molecule (1) is in equilibrium with neighboring molecules, whereas molecule (2) is in equilibrium with molecules along the surface but experiences a pulling force to the interior of the liquid mass.

TABLE 2-3 Surface Energy of Selected Materials

Solids	Surface Energy (mJ/m ²)	Liquids	Surface Energy (mJ/m ²)
Enamel ¹	92	Water ⁵	72.8 @25°C
Dentin ¹	87	Mercury ⁵	486 @25°C
Teflon ²	20	Saliva ⁶	53 @37°C
Gold alloy ³	51–54	Dentin bonding agent ⁷	34–55
Ni-Cr ³	48		
Commercial pure titanium ³	50		
Acrylic denture resins ⁴	46–54		

Note: Depending on the measuring methods and the materials used, the values obtained are likely to be different among studies. The table is intended to give readers a general idea of surface energies of selected materials.

¹Weerkamp AH, Uyen HM, Busscher HJ: Effect of zeta potential and surface energy on bacterial adhesion to uncoated and saliva-coated human enamel and dentin. *J Dent Res* 67:1483–1487, 1988.

²Jariczuk B, Białopiotrowicz T, Zdziennicka A: Some remarks on the components of the liquid surface free energy. *J Colloid Interf Sci* 211:96–103, 1999.

³Sardin S, Morrier JJ, Benay G, Barsotti O: In vitro streptococcal adherence on prosthetic and implant materials. Interactions with physicochemical surface properties. *J Oral Rehab* 31:140–148, 2004

⁴Sipahi C, Anil N, Bayramli E: The effect of acquired salivary pellicle on the surface free energy and wettability of different denture base materials. *J Dent* 29:197–204, 2001.

⁵Haynes WM, Lide DR, editors: *Handbook of chemistry and physics*, ed 91, Boca Raton, FL, 2011, CRC Press, pp 6–127.

⁶Glantz PO: The surface tension of saliva. *Odontol Rev* 21:119–127, 1970.

⁷Gonçalves M, Pécora JD, Vinha D, Silva RS: Surface tension of different dentin bonding resin systems. *Braz Dent J* 8:43–47, 1997.

array of neighbors surrounding it, and the potential energy is at a minimum. At the surface of the lattice, surface atom “2” is not equally attracted in all directions, and its potential energy is greater. This potential energy can be demonstrated by the behavior of a small drop of water placed on a clean glass slide. The water droplet spreads out and remains stationary when the glass slide is tilted or turned upside down. This means that the water molecules are attracted to the glass surface. This phenomenon of attraction can be explained by the potential energy discussed in Figure 2-2. The potential energy present is known as **surface energy** with the unit of mJ/m². Surface energy is also treated as the work required to generate a new surface.

In the case of a liquid, the molecules, which are shown as spheres in Figure 2-38, *B*, on the surface are pulled inward by the imbalanced forces generated by the unequal attraction on the surface. One good example is falling raindrops taking spherical shapes, which have the smallest surface area per volume of all known shapes. The sphere arrangement allows more molecules surrounded by their fellows (molecule “2” in Figure 2-38, *B*), while the molecules on the surface are constantly under tension. The reality is that the cohesive attraction between liquid molecules on the surface is the force keeping the surface to a minimum. This force is known as **surface tension**, which is often expressed as an amount of force exerted uniformly on a line of molecules of unit length along the surface. The most common unit is mN/m (millinewton per meter).

The terms surface energy and surface tension are often used interchangeably because the values of the two parameters are the same. Nonetheless, one should be aware that surface tension is used to define fluid surfaces, whereas surface energy is often used to define solid surfaces but is also applicable for liquids. Generally, the greater the cohesive force between atoms and molecules, the greater the surface energy of the surface. Table 2-3 lists the surface energy of selected solids and liquids.

Surfaces with a high surface energy are attractive to molecules of lower surface energy, such as hydrocarbons. Molecules in the air may be attracted to and become adsorbed on the material surface. Initially, the attraction between them is secondary bonding

(van der Waals force). As the distance between the molecules from the air and the surface diminishes, primary bonding may occur. Silver, platinum, and gold adsorb oxygen readily. Neither gold nor platinum forms stable oxides at room temperature; therefore the bond between oxygen and metals (gold and platinum) remains secondary. In the case of silver, silver oxide may form as oxygen becomes bonded to silver by covalent bonding. This process is called **chemisorption** and is limited to the monolayer of oxide present on the surface. Both phenomena constitute an adhesion process, where oxygen is the adhesive and metals are the adherents. Keep in mind that after interaction with oxygen, these surfaces are not pure metallic surfaces anymore in terms of surface bonding.

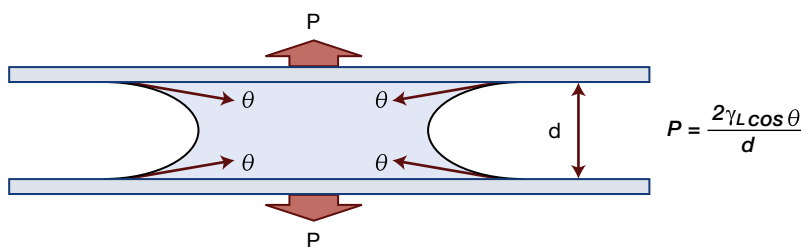
CRITICAL QUESTION

What conditions are necessary to achieve the strongest level of bonding?

Wetting

When two impurity-free glass slides are placed one on top of another and pressed together, they exhibit no tendency to adhere. Regardless of how smooth these glass surfaces may appear to be, they are likely to be rough on an atomic or molecular scale. Consequently, when they are placed in apposition, only the “hills” or high spots are in contact. Even if primary or secondary bonding occurs at these points of contact, these areas usually constitute only an insignificant portion of the total surface, and no perceptible adhesion takes place. In addition, no attraction is expected when the surface molecules of the attracting substances are separated by distances greater than 0.7 nm.

The examples of adhesives bonding to solid surfaces given earlier involved either gas or liquid. It is obvious that gas and liquid can adapt to a solid surface by flowing into surface irregularities to provide contact over a greater part of the surface of the solid. When a drop of water is introduced between two glass slides before they are pressed together, considerable difficulty is encountered



• **Figure 2-39** Two glass plates and water film. The liquid (water) between the two plates spreads because of good wetting. The attraction between the water molecule and glass surface is greater than the cohesive force between water molecules. Therefore, as water molecules spread, they also pull the two glass slides closer. Small arrows show the vector of surface tension, and broad arrows show the force that pulls the slides closer. The surface tension of water is about 72.8 mN/m. For a space of 1 μm , the stress acting on the slide will be 140 kN/m² (0.14 MPa). You will learn in Chapter 4 that the value is relatively low. Therefore, if the glass slides cannot be separated by pure tension, it is likely that the water film (d) is only nanometers in thickness.

in pulling the two slides apart (Figure 2-39). This is a result of the capillary action from intermolecular attractive forces between water and the glass plates.

To produce adhesion on any targeted surface, the liquid (adhesive) must spread and flow easily over the entire surface and attract to the solid. This characteristic is known as **wetting**. If the liquid beads up on the surface of the adherend, adhesion between the liquid and the adherend will be negligible or nonexistent. The ability to wet the substrate is the dominating contributor to the adhesive bond when the adhesive sets from liquid to solid.

The ability of an adhesive to wet the surface of the adherend is influenced by several factors. The cleanliness of the surface is of importance. Impurities on the solid surface often yield a surface of lower energy than the clean surface and prevent wetting by the adhesive, such as epoxy glue. A surface's surface energy can be so low, such as that of dental wax or Teflon, that it cannot be wet satisfactorily by most dental adhesives. Impurity-free metal surfaces, on the other hand, because of their high surface energy, interact vigorously with liquid adhesives.

In general, the comparatively low surface energies of organic and inorganic liquids permit them to spread freely on solids of high surface energy. This means the attraction between a liquid and a solid surface is greater than the cohesive forces of the liquids. This is a prerequisite of good wetting and strong adhesive joints.

CRITICAL QUESTION

Why does wetting increase (higher wettability) if the adhesive attraction at the liquid/solid interface is greater than the cohesive attraction of the liquid molecules?

Contact Angle of Wetting

How can we tell if a liquid wets a solid satisfactorily for bonding, especially when the surface to be bonded is covered by that very liquid? When we place one drop of water each on a clean glass slide, an acrylic plate, and a sheet of Teflon, we observe that the water drop spreads to the edge of the glass slide and to a lesser extent on the acrylic plate but appears to bead up on the Teflon surface. If we observe at the level of the solid substrate, we will see the symmetrical profile of the former water drop resting on a flat surface (Figure 2-40). Both ends of the profile depict where three phases—vapor (air), liquid (water), and solid (glass, acrylic, or Teflon)—converge. We can draw a tangent relative to the curvature

of the liquid profile from the vapor/liquid interface. The tangent line and the solid surface constitute an angle that defines the shape of the liquid; this is called the **contact angle**.

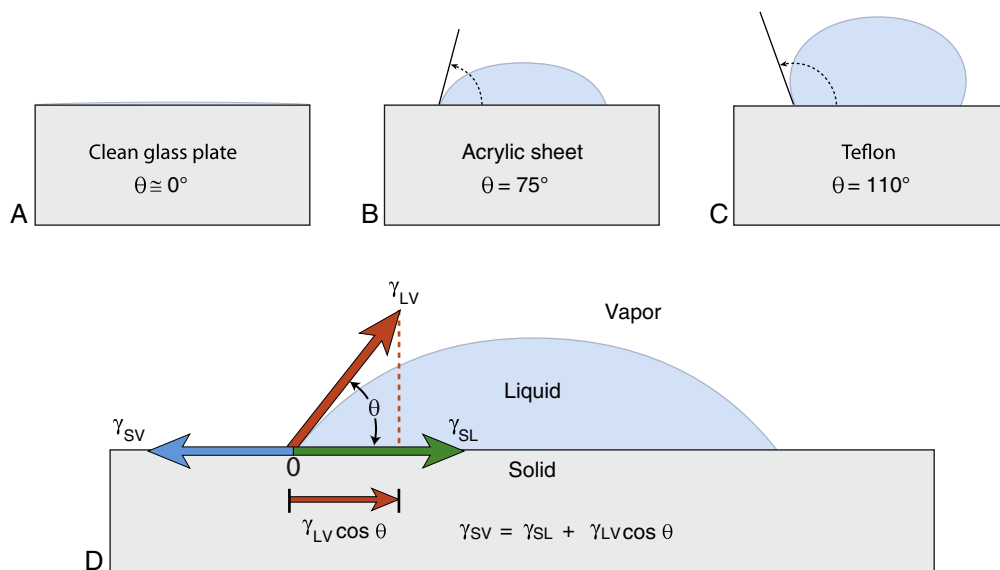
If the force of attraction between molecules of the adhesive and molecules of the substrate is stronger than the cohesive attraction (surface tension) between the molecules of the adhesive, the liquid adhesive will spread much more broadly over the solid surface and result in a smaller contact angle (Figure 2-40, A). Thus a small contact angle indicates that the adhesive forces at the interface are stronger than the cohesive forces holding the molecules of the adhesive together. If the adhesive beads up (Figure 2-40, C), the force of adhesion is weaker than the cohesive force of the adhesive. Because the tendency for the liquid to spread increases as the contact angle decreases, the contact angle is a useful indicator of spreadability or wettability (Figure 2-40, D). Complete wetting occurs at a contact angle of 0°, and no wetting occurs at an angle of 180°. Thus the smaller the contact angles between an adhesive and an adherend, the better the ability of the adhesive to flow into and fill in irregularities within the surface of the adherend. The fluidity of the adhesive influences the extent to which these voids or irregularities are filled.

If oil drops or liquids other than water have been used instead, the observed contact angle will be different. Therefore it is important to know the identity of the liquid that has been used to determine the contact angles. If none is identified in the literature, it is likely that distilled water has been used.

The profile of the liquid on a flat surface shows that there are three distinct interfaces, vapor/liquid, liquid/solid, and solid/vapor, and each interface is characterized by an interfacial energy, γ_{VL} , γ_{LS} , and γ_{SV} , respectively. At equilibrium, the interfacial energies among the three phases along x -axis should follow Young's equation, shown in Figure 2-40, D. The equation shows that there are two routes of decreasing contact angle; one is to have a high-surface-energy solid surface, and the other is to use a low-surface-tension liquid. It is important to point out that Young's equation shown in Figure 2-40 assumes a perfectly flat surface at the molecular level, and any surface roughness and impurities can cause a deviation in the values of contact angle calculated by Young's equation.

CRITICAL QUESTION

You observe a lack of soft or hard tissue details in a gypsum model you have made from a hydrophobic impression material. What steps can be taken to eliminate this problem when you are using this impression material in the future?



• **Figure 2-40** Contact angles of distilled water on three surfaces and relationship among interfacial energy. **A**, Water spreads freely on a flame-cleaned glass slide (good wetting). The profile depicted here is considered to have a 0° contact angle. **B**, Water on an acrylic surface. **C**, Water on a Teflon surface (poor wetting). **D**, Relationships between the interfacial energies at vapor/liquid (γ_{LV}), liquid/solid (γ_{LS}), and solid/vapor (γ_{SV}) interfaces with respect to contact angle at equilibrium; the relationship is also known as *Young's equation*.

Issues of wetting associated with individual material occur daily in clinical dentistry and are discussed in later chapters. Here is one example of interest. When gypsum products discussed in [Chapter 13](#) are mixed with water to pour dental models on various types of impressions, wetting must occur between gypsum and the impression to ensure good surface quality of the gypsum model. The basic ingredient of the most popular silicone-based elastomeric impression material today is hydrophobic because a contact angle of greater than 90° is observed when an aqueous medium is poured into this elastomeric mold. To improve the wettability of the set impression material by a gypsum–water mixture, the operator usually sprays a *surfactant* (also called *debubbler*) on the impression before pouring. The most direct approach by the manufacturer is to incorporate a **wetting agent** (also known as a surfactant) in the impression material during the manufacturing process ([Chapter 13, Wettability of Impression Materials and Hydrophilization of PVS](#)). The wetting agent migrates to the solid surface and accommodates surface wetting by the aqueous gypsum-forming mixture. One may think that surfactant increases the surface energy of the impression material. The fact is just the opposite. The surfactant on the solid surface dissolves in the water of the gypsum product that reduces the cohesive attraction between water molecules and, thus, lowers the contact angle of the gypsum slurry on the impression surface. [Table 2-4](#) lists contact angles of probing liquids on selected materials.

CRITICAL QUESTION

Micromechanical bonding of resin sealant to tooth enamel is usually quite effective in preventing pit and fissure areas from tooth decay. However, many factors can reduce the bonding effectiveness, resulting in partial or total loss of the sealant. Which of these factors are possible causes of debonding?

Mechanical Interlocking

Strong attachment of one substance to another can also be accomplished by mechanical means rather than by molecular attraction. Such structural retention may be crude, as evidenced by some nondental applications involving the use of screws, bolts, or undercuts. Similar procedures that involve more subtle mechanisms are also used in restorative dentistry and are called *mechanical interlocking* or *bonding*.

Before resin-based adhesives were introduced to dentistry, various types of pastes or slightly viscous materials, like zinc phosphate cement ([Chapter 7, Zinc Phosphate Cement](#)), were being used to retain cast gold alloy crowns or base metal endodontic posts and cores. These materials do not form a strong molecular attraction to the substrate surface, but they provide the needed retention to hold the prostheses in place. In this scenario, the luting medium penetrates irregularities that exist on the intaglio of the casting and those that are present on the adjoining tooth structure. Upon hardening, the numerous cementing material projections embedded in the adherend surface provide the anchorage for mechanical retention. This process is often called **micromechanical bonding**. Good wetting is necessary to ensure penetration.

The early versions of resin-based filling materials did not form a strong attraction to tooth structure, and consequently, leakage adjacent to the restoration occurred. Such leakage patterns contribute to marginal stain, secondary caries, and irritation of the pulp. This drawback was brought under control only when acid etching of enamel had been accepted as a routine procedure. Before insertion of the resin, the enamel of the adjoining tooth structure is exposed to phosphoric acid for a short period, and then rinsed to remove any residual acid. The acid produces minute irregularities on the enamel surface, into which the resin flows when it is placed into the tooth preparation. On hardening, these resin projections provide improved mechanical retention of the

TABLE 2-4 Contact Angles of Probing Liquids on Solid Surfaces

Solid	Probing Liquid	Contact Angle (degree)	Impression Materials	Probing Liquid	Contact Angle (degree)
Amalgam ¹	Mercury	145	Polyether ⁵	Water	30–44
Amalgam ²	Water	77	Polysulfide ⁵	Gypsum solution (0.2 gm/mL)	76–85
Acrylic denture resins ²	Water	75	Addition silicone ⁵	Water	34–105
Dental ceramic (feldspathic core) ³	Water	71	Addition silicone (hydrophilic) ⁵	Water	20–78
Dental ceramic (feldspathic core) ³	Bonding resin	54	Condensation silicone ⁵	Water	82–103
Teflon ²	Water	110			
Commercial pure titanium ⁴	Water	54			

Note: Depending on the measuring methods and the materials used, the values obtained are likely to be different among studies. The table is intended to give readers a general idea of the contact angles of various dental materials.

¹Baran G, O'Brien WJ: Wetting of amalgam alloys by mercury. *JADA* 94:898–900, 1977.

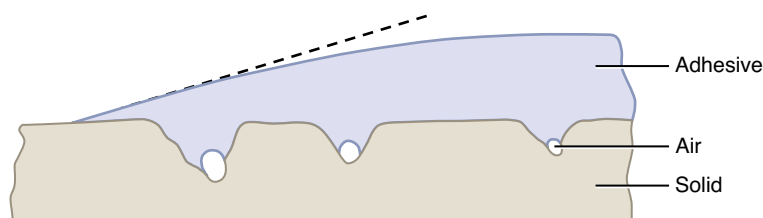
²O'Brien WJ: Capillary penetration of liquids between dissimilar solids. PhD Dissertation, University of Michigan, 1967.

³Oh W, Shen C, Alegre B, Anusavice KJ: Wetting characteristic of ceramic to water and adhesive resin. *J Prosthet Dent* 88:616–621, 2002.

⁴Ponsonnet L, Reybier K, Jaffrezic N, et al: Relationship between surface properties (roughness, wettability) of titanium and titanium alloys and cell behavior. *Mat Sci Eng C* 23:551–556, 2003.

⁵Cullen DR, Mikesell JW, Sandik JL: Wettability of elastomeric impression materials and voids in gypsum casts. *J Prosthet Dent* 66:261–265, 1991.

⁶Pratten DH, Craig RG: Wettability of a hydrophilic addition silicone impression material. *J Prosthet Dent* 61:197–201, 1989.



• **Figure 2-41** Air pockets form in a surface irregularity even when the contact angle of the adhesive is low. These voids contribute to the propagation of adhesive failure by concentration of stresses.

restoration, thereby reducing the possibility of interfacial leakage. In fact, the etching procedure cleans the enamel surface and creates more surface area, facilitating greater wettability of the enamel by the adhesive and, subsequently, a stronger bond.

It is important to note that whereas surface imperfections provide sites for mechanical bonding, there are areas that adhesives may not fill because of trapped air pockets (Figure 2-41). When the adhesive interfacial region is subjected to thermal changes and mechanical stresses, stress concentrations develop around these voids. The stress may become so great that it initiates a separation in the adhesive bond adjacent to the void. This crack may propagate from one void to the next, and the joint may separate under stress.

CRITICAL QUESTION

What are the main challenges involved in bonding to tooth structure?

Bonding to Tooth Structure

Adhesive bonding to tooth structure and other dental materials has become a major component of restorative dentistry. So far, we have used an ideal adherend that has a clean surface with uniform composition and certain surface irregularities in our discussion of bonding. Tooth structure does not fall into that category. Tooth composition is heterogeneous. Both organic and inorganic

components are present in different amounts in dentin compared with enamel. A material that can adhere to the organic components may not adhere to the inorganic components, and an adhesive that bonds to enamel may not adhere to dentin to the same extent.

The instruments used to prepare the tooth for bonding leave a rough surface and debris, which promote air entrapment at the interface. Such prepared surfaces are routinely treated with appropriate agents to remove the debris. New debris must be removed after each additional procedure, in addition to dealing with saliva contamination. Furthermore, there is a fluid exchange through certain components of the tooth. The dental adhesive must compete with water for wetting the tooth surface by displacing or incorporating it. Then, too, the adhesive must sustain long-term adhesion to the tooth structure in an aqueous environment. Attempts are being made to use more hydrophilic resins that are not as sensitive to the presence of moisture as materials currently in use. To further enhance adhesive bonding to tooth structure or other dental materials, the incorporation of functional groups that have the potential of chemically reacting with the bonding substrate is also being sought. Perhaps there will be no need for mechanical retention in the cavity preparation in the future. Keeping the surface free of contamination remains a vital part of bonding procedures. These subjects are discussed in detail in [Chapter 6, Mechanisms of Adhesion and Acid-Etch Technique](#), which deals with materials for bonding applications.

Selected Readings

Abbaschian R, Abbaschian L, Reed-Hill RE: *Physical Metallurgy Principles*, ed 4, Stamford CT, 2009, Cengage Learning.

An excellent textbook on physical metallurgy that discusses the solidification of metals and alloys and the formation of equiaxed polycrystalline and dendritic microstructures.

Brantley WA, Cai Z, Carr AB, et al: Metallurgical structures of as-cast and heat-treated high-palladium dental alloys, *Cells Mater* 3:103–114, 1993.

High-palladium alloys with equiaxed polycrystalline and dendritic microstructures are described. Careful study of the micrographs is useful for comparing the potential structural integrity and some properties of these alloys.

Buonocore MG: *The Use of Adhesives in Dentistry*, Springfield, IL, 1975, Charles C Thomas.

The problems associated with dental adhesives are nicely illustrated. It is of interest that many of the procedures using bonding technology discussed in this text have become commonplace.

Cowie JMG, Arrighi V: *Polymers: Chemistry and Physics of Modern Materials*, ed 3, Boca Raton, FL, 2007, CRC Press.

Emphasizes structure/property relationships in polymers. Written for nonchemists who require a brief, readable introduction to polymer chemistry.

Good RJ: Contact angle, wetting, and adhesion: a critical review, *J Adhes Sci Technol* 6:1269–1302, 1992.

An excellent review on the fundamentals of contact angle and wetting and their relationship to adhesion.

Habib E, Wang R, Wang Y, et al: Inorganic fillers for dental resin composites: Present and future, *ACS Biomater Sci Eng* 2:1–11, 2016.

Pampuch R: *An Introduction to Ceramics. Lecture Notes in Chemistry*, Vol. 86, 2014, Springer International Publishing.

Rueggeberg FA: From vulcanite to vinyl, a history of resins in restorative dentistry, *J Prosthet Dent* 87:364–379, 2002.

A comprehensive review of the introduction and evolution of polymeric materials in modern dentistry.

Söderholm K-JM: Coatings in dentistry—A review of some basic principles, *Coatings* 2:138–159, 2012.

This paper reviews fundamental principles of surface properties/adhesives since these topics form the foundation for most coating procedures used in dentistry.

Van Vlack LH: *Elements of Materials Science and Engineering*, ed 6, Reading, MA, 1989, Addison-Wesley.

An excellent primer on materials science. Chapter 5 describes phase diagrams, and Chapters 8 and 9 present deformation and strengthening mechanisms for alloys.

Full Selected Readings for this chapter can be found on www.expertconsult.com.

Selected Reading (Web Version)

Structure of Matter

Callister WD, Jr, Rethwisch DG: *Materials Science and Engineering: An Introduction*, ed 8, Hoboken, NJ, 2010, John Wiley & Sons.

An excellent text on materials science for a more in-depth coverage of materials structure and properties.

Gordon JE: *The New Science of Strong Materials, or Why You Don't Fall Through the Floor?* ed 2, Princeton, NJ, 1984, Princeton University Press. A general discussion of the strength of materials from a fundamental base. The sections on biological structural materials, timber, cellulose, teeth, and bone are particularly interesting.

Van Vlack LH: *Elements of Materials Science and Engineering*, ed 6, Reading, MA, 1989, Addison-Wesley.

An excellent primer on materials science. Chapter 5 describes phase diagrams, and Chapters 8 and 9 present deformation and strengthening mechanisms for alloys.

Metal

Abbaschian R, Abbaschian L, Reed-Hill RE: *Physical Metallurgy Principles*, ed 4, Stamford, CT, 2009, Cengage Learning.

An excellent textbook on physical metallurgy that discusses the solidification of metals and alloys and the formation of equiaxed polycrystalline and dendritic microstructures.

Brantley WA, Cai Z, Carr AB, et al: Metallurgical structures of as-cast and heat-treated high-palladium dental alloys, *Cells Mater* 3:103–114, 1993.

High-palladium alloys with equiaxed polycrystalline and dendritic microstructures are described. Careful study of the micrographs is useful for comparing the potential structural integrity and some properties of these alloys.

Brantley WA, Cai Z, Vermilyea SG, et al: Effects of solidification conditions and heat treatment on the microstructure and Vickers hardness of Pd-Cu-Ga dental alloys, *Cells Mater* 6:127–135, 1996.

This article shows that the incidence of hot tears in a high-palladium alloy with a dendritic as-cast microstructure is much greater when the alloy is quenched rather than bench-cooled. The path of crack propagation is between adjacent interdendritic regions.

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This article discusses the formation of hot tears in a high-palladium alloy with a dendritic as-cast microstructure and the potential role of burnout temperature on their formation.

Cullity BD: *Principles of X-Ray Diffraction*, ed 2, Reading, MA, 1978, Addison-Wesley.

A description of x-ray diffraction techniques used to determine crystal structures of metallic materials. Chapter 13 in this book summarizes the ordered structures in gold-copper alloys.

Flinn R, Trojan P: *Engineering Materials and Their Applications*, ed 3, Boston, MA, 1986, Houghton Mifflin, pp 116–169.

A discussion of equilibrium [phase diagram] and nonequilibrium conditions in systems as related to properties. There are excellent photographs and examples.

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A comprehensive reference book on the structure, properties, and processing of metals. This book also describes testing methods for metals and provides an excellent review of fractographic analysis procedures for the study of fractured metals.

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The characteristic submicron tweed structure and microtwins in these alloys are described.

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3

Physical and Chemical Properties of Solids

OUTLINE

Rheology

Structural Relaxation

Thermal Properties

Electrochemical Properties

Magnetic Materials

KEY TERMS

RHEOLOGY

Dilatant Resistance to flow increases as the rate of deformation (shear strain rate) increases. The more rapidly dilatant fluids are stirred or forced through a syringe, the more viscous (thicker) and more resistant to flow they become.

Pseudoplastic Viscous character that is opposite from dilatant behavior in which the rate of flow decreases with increasing strain rate until it reaches a nearly constant value. Thus the more rapidly pseudoplastic fluids are stirred or forced through a syringe, the less viscous (thinner) and more easily they flow.

Rheology Study of the deformation and flow characteristics of matter (see *viscosity*).

Thixotropic Property of gels and other fluids to become less viscous and flow when subjected to steady shear forces through being shaken, stirred, squeezed, patted, or vibrated. When the shear force is decreased to zero, the viscosity increases to the original value over a short time delay.

Viscosity Resistance of a fluid to flow (see *rheology*).

STRUCTURAL RELAXATION

Creep Time-dependent plastic strain of a solid under a static load or constant stress.

Sag Irreversible (plastic) deformation of metal frameworks of fixed dental prostheses in the firing temperature range of ceramic veneers.

COLOR AND OPTICAL EFFECTS

Absorption The extent to which light is absorbed by the material in an object.

Chroma Degree of saturation of a particular hue (dominant color).

Color Sensation induced from light of varying wavelengths that reaches the eye.

Esthetics Principles and techniques associated with the development of the color and appearance required to produce a natural, pleasing effect in the dentition.

Hue Dominant color of an object (e.g., red, green, or blue).

Metamerism Phenomenon in which the color of an object under one type of light source (e.g., room light) appears to change when illuminated by a different light source (e.g., sunlight).

Opacity The extent to which light does not pass through a material. No image and no light can be seen through an opaque object.

Reflection The amount of light that reflects from the surface of an object.

Refract/Refraction The degree to which light is bent when it passes from one medium to another. This makes a spoon appear bent in a glass of drinking water when light passes from air through glass into water, reflects from the spoon, and then passes back through water and glass into air. The index of refraction is a measure of this effect.

Translucency Property of an object in which light is scattered as it passes through, revealing a diffuse image.

Transmit/Transmission The amount of light passing through an object.

Transparency The extent to which light passes through a material and to which an undistorted image can be seen through it.

Value Relative lightness or darkness of a color. Also known as *luminous reflectance* and the *gray scale*.

THERMAL PROPERTIES

Coefficient of thermal expansion (linear coefficient of expansion) Change in length per unit of the original length of a material when its temperature is raised by 1 K.

Kelvin (K) The kelvin (K) temperature scale extends the degree Celsius scale such that zero degrees K is defined as absolute zero ($= -273.15^{\circ}\text{C}$). Temperatures on this scale are called "kelvins," not "degrees kelvin," kelvin is not capitalized, and the symbol (capital K) stands alone with no degree symbol; $1\text{ K} = 1^{\circ}\text{C}$, $\text{K} = ^{\circ}\text{C} + 273.15$.

Thermal conductivity (coefficient of thermal conductivity) Property that describes the thermal energy transport in watts per second through a material 1 cm thick with a cross-sectional area of 1 cm^2 when the temperature differential between the surfaces of the material perpendicular to the heat flow is 1 K.

Thermal diffusivity Measure of the speed with which a temperature change will proceed through an object when one surface is heated.

ELECTROCHEMICAL PROPERTIES

Concentration cell Electrochemical corrosion cell in which the potential difference is associated with the difference in concentration of a dissolved species, such as oxygen, in solution along different areas of a metal surface. Pitting corrosion and crevice corrosion are types of concentration cell corrosion.

Corrosion Chemical or electrochemical process in which a solid, usually a metal, is attacked by an environmental agent, resulting in partial or complete dissolution.

Electromotive series Arrangement of metals by their equilibrium values of electrode oxidation potential. Used to judge the tendency of metals and alloys to undergo electrochemical (galvanic) corrosion.

Galvanic corrosion (electrodeposition) Accelerated attack occurring on a less noble metal when electrochemically dissimilar metals are in electrical contact within a liquid corrosive environment.

Galvanic shock Pain sensation caused by the electrical current generated when two dissimilar metals are brought into contact in the oral environment.

Stress corrosion Degradation caused by the combined effects of mechanical stress and a corrosive environment, usually exhibited as cracking.

Tarnish Process by which a metal surface is dulled or discolored when a reaction with a sulfide, oxide, chloride, or other chemical causes surface discoloration through the formation of a thin oxidized film.

MAGNETIC MATERIALS

Magnet Metallic material in which the component atoms are so ordered that it attracts iron-containing objects or aligns itself in an external magnetic field.

Tesla Unit of flux density (T) of the magnetic field produced by a magnet.

Every dentist in the process of making or delivering a restoration must select various materials to complete the task. In making the choice, the dentist must have a thorough knowledge of the properties and behavioral characteristics of the materials chosen, namely, the physical and chemical properties. *Physical properties* are based on the laws of mechanics, acoustics, optics, thermodynamics, electricity, magnetism, radiation, atomic structure, and nuclear phenomena. *Chemical properties* are based on the ways in which substances interact, combine, and change at the molecular level, as governed by their outer orbital electrons.

From the categories of dental materials and challenges discussed in Chapter 1, there are specific behaviors of the materials during processing and use that dentists should consider, such as the flowability (or formability), esthetic appearance, thermal expansion, chemical durability, and magnetism of the materials. As examples, flow and viscosity (the resistance of a fluid to flow) are essential properties for mixing direct restorative materials (Chapter 1, *Direct Restorative Materials*) and gypsum products and impression materials (Chapter 13). Creep (slow deformation under a static load) is relevant to the clinical performance of amalgam (Chapter 8, *Creep*) and the fabrication of metal-ceramic prostheses (Chapter 10, *Requirements of Metal Component*). The physical properties of color and thermal expansion are of particular importance to the performance of all restorations, especially for dental ceramics (Chapter 10, *Physical Properties*). Tarnish and corrosion are electrochemical properties that strongly affect the performance of metals and their alloys (Chapters 8 and 9). Magnetic-able prostheses materials are often used for retaining implant-borne prostheses and for orthodontic tooth movement in place. Mechanical properties, a subset of physical properties based on the laws of mechanics, are discussed in Chapter 4.

These phenomena will be discussed in greater detail in later chapters. However, having a firm grasp of the underlying principles that govern the properties is critical.

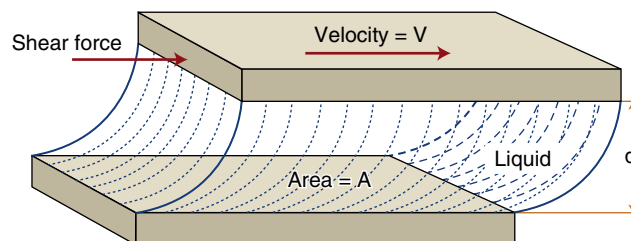
Rheology

Rheology is the study of the deformation and flow characteristics of matter under stress, whether liquid or solid. Dental professionals must manipulate a wide variety of dental materials in a fluid state to achieve successful clinical outcomes. Moreover, the manipulation

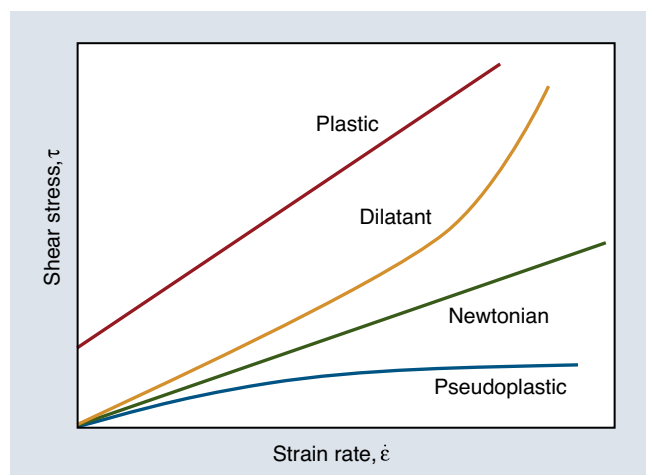
and handling of a given material in the liquid state determine this material's performance as a solid. Most dental materials are initially in a fluid state so that they can be placed and shaped as required; then they undergo transformation to a solid state, in which they are durable and perform their function. Cements and impression materials undergo a fluid-to-solid transformation in the mouth. Gypsum products used in the fabrication of models and dies are transformed extraorally from fluid slurries into solids (see Chapter 13, *Gypsum Products*).

Although a liquid at rest cannot support a shear stress (shearing force per unit shearing area), most liquids, when placed in motion, resist imposed forces that cause them to move. This resistance to fluid flow, termed **viscosity**, is controlled by internal frictional forces within the liquid. Thus viscosity is a measure of the consistency of a fluid and the fluid's resistance to flow. Therefore highly viscous fluids flow slowly. Dental materials exhibit differing viscosities depending on their intended clinical application. In everyday life, we find wide differences in viscosities among such fluids as water, syrup, ketchup, moisturizing cream, and toothpaste. We will be discussing dental materials of various viscosities in later chapters.

The concept of viscosity is illustrated in Figure 3-1. A liquid occupies the space between two flat surfaces, such as when a spatula is moved through a pasty fluid, for example, a dental cement, to blend two components on a mixing pad. The mixing surface is fixed, and the upper surface (e.g., a spatula blade) moves to the right at a given velocity (V) with sufficient force (F) to overcome



• **Figure 3-1** Shear strain, $\hat{\epsilon} (= V/d)$ of a viscous liquid between two plates caused by translation of the top plate at a velocity, V , relative to the stationary lower plate. This illustrates, for example, a spatula blade mixing dental cement on a mixing pad.



• **Figure 3-2** Shear stress versus shear strain rate for fluids exhibiting different types of rheological behaviors.

the frictional resistance within the fluid and cause the fluid to flow. As discussed in [Chapter 1, What Is Force?](#), stress is the force per unit area that develops within a structure when an external force is applied. If the two surfaces have an area (A) in contact with the liquid, a shear stress (τ) can be defined as $\tau = F/A$. The shear strain rate is $\dot{\epsilon} = V/d$, where d is the shear distance of the upper surface relative to the fixed lower surface, and V is the velocity of the moving surface. As the shear stress τ increases, $\dot{\epsilon}$ increases, and a curve can be obtained for shear stress versus strain rate.

The rheologic behaviors of four types of fluids are shown in [Figure 3-2](#). Curves depicting shear stress versus shear strain rate are used to characterize the viscous behavior of fluids, and the viscosity (η) is defined as the shear stress divided by the strain rate, $\eta = \tau/\dot{\epsilon}$. The straight line from the origin in [Figure 3-2](#) shows that the force applied is proportional to the strain rate of the fluid. This is known as *Newtonian viscosity*. A Newtonian fluid has a constant viscosity independent of the strain rate. Viscosity is measured in units of pascal second (Pa·s) or centipoise (cP; 1 Pa·s = 10,000 cP). Pure water at 20 °C has a viscosity of 1.0 cP, whereas the viscosity of molasses is approximately 300,000 cP (30 Pa·s). This value is similar to that of tempered agar hydrocolloid impression material (281,000 cP or 28.1 Pa·s at 45 °C). Of the elastomeric impression materials, light-body (“thin” consistency) polysulfide has a viscosity of 109,000 cP (10.9 Pa·s), compared with 1,360,000 cP (136 Pa·s) for heavy-body (“thick” consistency) polysulfide at 36 °C. The viscosity of most fluids decreases rapidly with increasing temperature, which is the reason the reported values for material viscosity often include the temperature at measurement.

The viscosity of many dental materials decreases with increasing strain rate until the viscosity reaches a nearly constant value. That is, the faster materials are stirred, forced through a syringe, or squeezed, the less viscous and more fluid they become. This is called **pseudoplastic** viscosity and is illustrated by the change in the slope of the plot in [Figure 3-2](#). Liquids that show the opposite behavior are **dilatant** and become more rigid as the rate of deformation (shear strain rate) increases. That is, the faster they are stirred, squeezed, and so forth, the more viscous and resistant to flow they become. Some classes of materials behave like a rigid body until some minimum value of shear stress is reached. This is represented by the offset along the shear-stress axis. These fluids, which exhibit rigid behavior initially and then attain constant viscosity, are referred to as “plastic.” Ketchup is a familiar example—a sharp blow to the bottle is usually required to produce an initial flow.

Viscosity may also depend on the previous deformation of the liquid. **Thixotropic** fluids become less viscous upon repeated applications of pressure and stay at that lower viscosity for a short period of time before the viscosity of the previous state is regained. Dental prophylaxis pastes, plaster of Paris, resin cements, and some impression materials are thixotropic. The thixotropic nature of impression materials is beneficial because the material dispensed from the syringe will maintain a lower viscosity for a while, allowing better wetting of the tissue. The material then stops moving when a state of higher viscosity is regained. For instance, prophylaxis paste does not flow out of a rubber cup until this is rotated against the teeth to be cleaned. For pseudoplastic materials, the material regains the viscosity as soon as the stressing stops.

Structural Relaxation

Structural relaxation is a rheological phenomenon of solids that occurs so slowly that it is not noticed until the process completes. The two categories of interest in dentistry are (1) stress relaxation and (2) creep and flow.

Stress Relaxation

After an object or substance has been permanently deformed, a process of shape changing by force, the atoms and molecules are displaced and are no longer in equilibrium positions. There are trapped internal stresses that make the structure unstable. The substance can relieve these stresses through a solid-state diffusion process driven by thermal energy, where the atoms can slowly return to their equilibrium positions. The result is a change in the shape or contour of the solid as the atoms or molecules change positions. The process is known as *stress relaxation* and may cause warping or distortion of the object. Such stress relaxation can occur with elastomeric impression materials and can lead to distortions in the impression and a subsequent lack of fit of the prostheses, as discussed in [Chapter 13, Elasticity and Viscoelasticity](#).

The rate of relaxation increases with an increase in temperature. For example, if a wire is bent, the wire may tend to straighten out if it is heated to a high temperature. At room temperature, any such relaxation caused by the rearrangement of metal atoms may be negligible. On the other hand, there are many noncrystalline dental materials (e.g., waxes, resins, and gels) that, when manipulated and cooled, can then undergo relaxation (with consequent distortion) at a slightly elevated temperature.

Creep and Flow

If a solid metal is held at a temperature near this metal’s melting point and is subjected to a constant load, the resulting strain will increase over time. **Creep** is defined as the time-dependent plastic strain of a material under a static load or constant stress. Metals for cast restorations or metal-ceramic prostheses have melting points (for pure metals) or melting ranges (for alloys) that are much higher than mouth temperatures, and they are not susceptible to creep deformation intraorally. However, some alloys used for long-span metal-ceramic bridge structures can sag under the influence of the mass of the prosthesis at porcelain-firing temperatures. This phenomenon is discussed further in [Chapter 9, Requirements of Alloys for Metal-Ceramic Applications](#).

Dental amalgams, because of their mercury content, begin melting at temperatures a few hundred degrees above room temperature. Because of amalgam’s low melting range, this material can undergo creep at a restored tooth site under periodic sustained

stress, such as would be imposed by patients who clench their teeth. Because creep produces continuing plastic deformation, the process can, over time, be very destructive to a dental amalgam filling. The relationship of this property to the behavior of amalgam restorations is discussed in [Chapter 8, Creep](#).

The term *flow*, rather than *creep*, has generally been used in dentistry to describe the rheology of amorphous materials such as waxes ([Chapter 13, Flow of Dental Wax](#)). The flow of wax is a measure of the potential to deform under a small static load, which includes its own mass. Creep or flow characteristics are determined using a cylinder of prescribed dimensions subjected to a given compressive load for a specified time and temperature. The creep or flow is measured as the percentage decrease in length that occurs under these testing conditions. Creep may cause unacceptable deformation of dental restorations (e.g., low-copper dental amalgam) made from a material that is used clinically at a temperature near its melting point for an extended period.

Color and Optical Effects

Esthetic considerations in restorative and prosthetic dentistry have received increasingly greater emphasis in recent decades, and the challenges have grown even greater in the past few years following the widespread use of bleaching and whitening technologies. Thus the development of a general-purpose, technique-insensitive, direct-filling, tooth-colored, color-stable restorative material remains one of the more serious challenges of current dental materials research.

Because esthetic dentistry imposes severe demands on the artistic abilities of the dentist and technician, knowledge of the underlying scientific principles of color and other optical effects

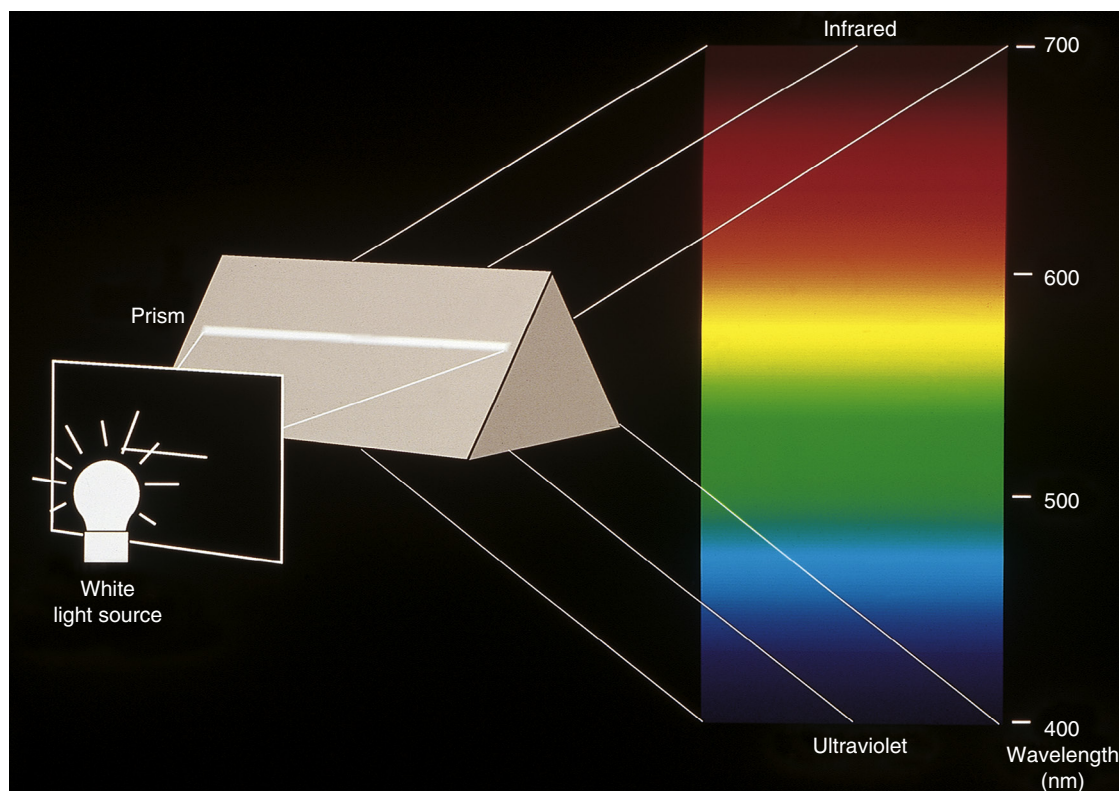
is essential. This is especially true for the increasingly popular restorations that involve ceramic materials (see [Chapter 10, Color Matching Ability and Aesthetic Qualities](#)).

Nature of Light and the Role of Human Vision

Light is electromagnetic radiation that can be detected by the human eye. The eye is sensitive to wavelengths from approximately 400 nm (violet) to 700 nm (dark red), as shown in [Figure 3-3](#). For an object to be visible, this object must reflect or **transmit** incident light from an external source. The incident light is usually polychromatic, that is, a mixture of the various wavelengths, commonly known as “white” light. Incident light is selectively absorbed or scattered (or both) at certain wavelengths. The spectral distribution of the transmitted or reflected light resembles that of the incident light, although certain wavelengths are reduced in magnitude.

The phenomenon of vision, and certain related terminology, can be illustrated by considering the response of the human eye to light reflected from an object. Light from an object that is incident on the eye is focused in the retina and is converted into nerve impulses, which are transmitted to the brain. The retina has two types of cells that gather light: rods and cones. The rods are around the outer ring of the retina and are active in dim light. Cone-shaped cells in the retina are responsible for color vision.

Signals from the retina are processed by the brain to produce the psychophysiological perception of color. Because a neural response is involved in color vision, constant stimulation by a single color may result in color fatigue and a decrease in the eye's response. Defects in certain portions of the color-sensing receptors result in the different types of color blindness; thus



• **Figure 3-3** Spectrum of visible light ranging in wavelength from 400 nm (violet) to 700 nm (red). The most visually perceptible region of the equal energy spectrum under daylight conditions is between 540 and 570 nm, with a maximum value of visual perceptibility at 555 nm.

humans vary greatly in their ability to distinguish colors. In a scientific sense, one might liken the normal human eye to an exceptionally sensitive differential colorimeter, a scientific instrument that measures the intensities and wavelengths of light. Although colorimeters are more precise than the human eye in measuring slight differences in colored objects, they are inaccurate for rough or curved surfaces. The eye is highly sensitive in comparing two colors seen side by side, whether on rough, smooth, flat, or curved surfaces.

The Nature of the Object Under View

Esthetics is critically important in dealing with dental restorative materials. For good esthetics, the interaction of light with restorative materials must mimic the interaction of light with natural teeth. The nature of the restorative material, or that of any object under view, determines how that object will appear. Electromagnetic radiation in the visible region interacts with an object through **reflection** from the surface, **absorption**, **refraction**, or **transmission** (i.e., by passing through unchanged). These phenomena determine the **opacity**, **translucency**, or **transparency** of an object. Light reflected from rough surfaces *scatters* in many directions because light is reflected at many angles by the uneven surface. This leads to an appearance that ranges from mirrorlike for a perfectly smooth surface (termed *specular reflectance*) to the flat, dull appearance (termed *diffuse reflectance*) of a surface such as chalk.

The opacity of a material is related to the amount of light the material can absorb and/or scatter. The opposite of opacity is translucency. For example, if 1-mm thicknesses of each of two materials absorb light passing through them, the material that

absorbs 20% of the light is less opaque and more translucent than the material that absorbs 50%. Transparent materials are at the far end of the translucency scale, absorb no light, and transmit 100% of the light that passes through them.

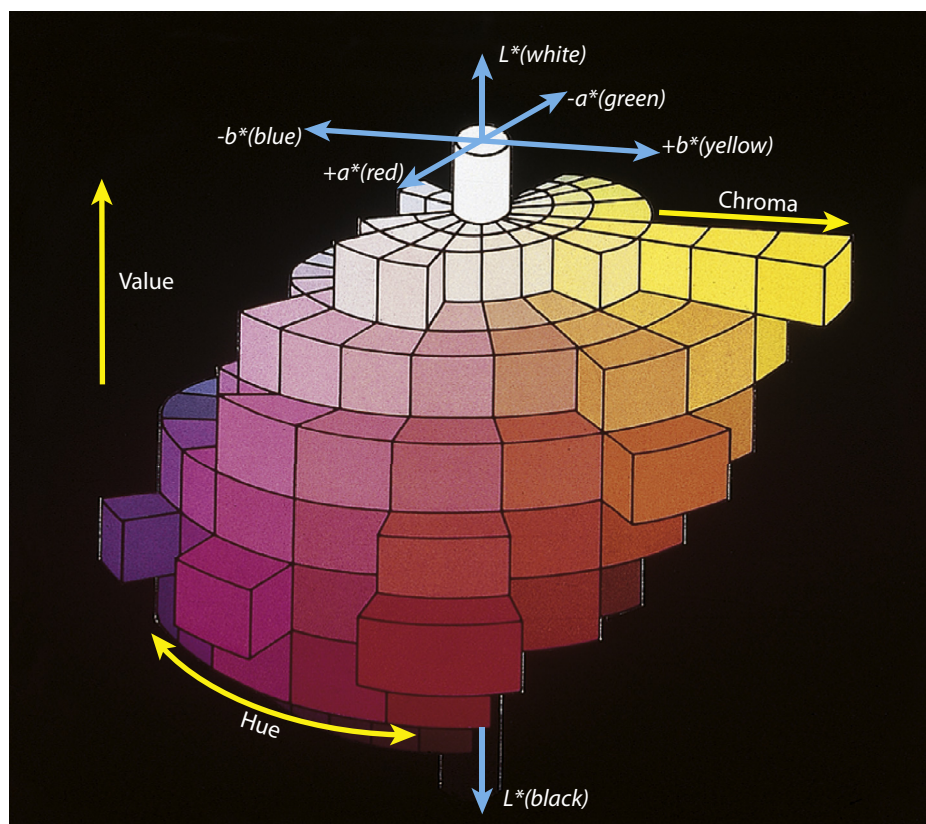
Enamel is a composite material consisting of hydroxyapatite crystals in a protein matrix. When light strikes enamel, some is reflected, some refracted, some absorbed, and some transmitted. Enamel has a refractive index of 1.65 and is translucent.

CRITICAL QUESTION

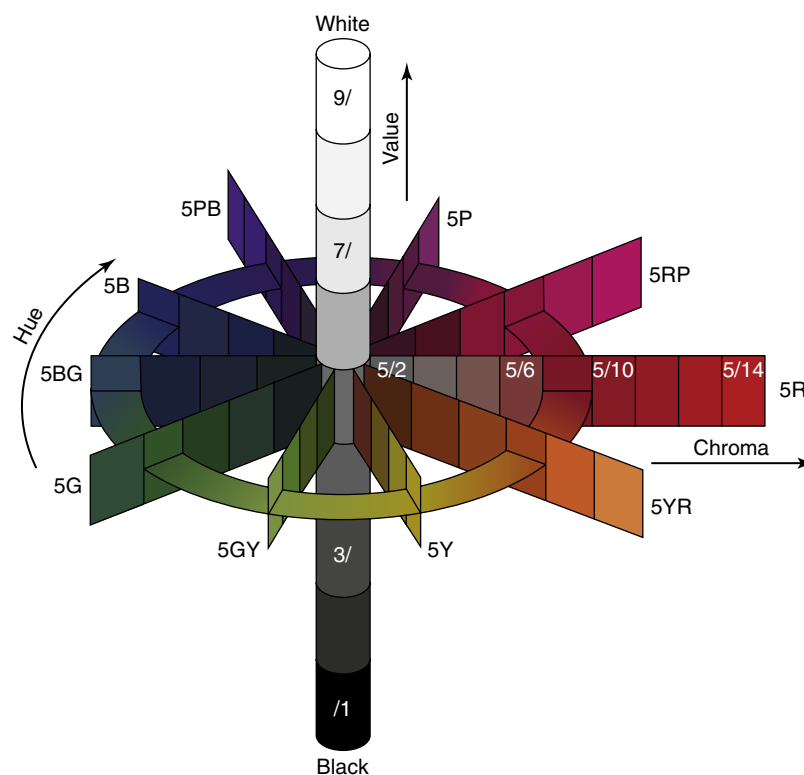
How is color described objectively and quantitatively?

Three Dimensions of Color

Verbal descriptions of color are not precise enough to describe the appearance of teeth. For example, the definition of *puce* is “a brilliant purplish-red color,” according to Microsoft’s *Encarta World English Dictionary*, whereas *Webster’s Third New International Dictionary* defines *puce* as “a dark red that is yellower and less strong than cranberry, paler and slightly yellower than average garnet, bluer, less strong, and slightly lighter than pomegranate, and bluer and paler than average wine.” These definitions are too variable, complex, and imprecise to describe a desired color of a dental crown to a laboratory technician. Such a written description is subjective and does not clearly and unambiguously allow someone to perceive the color. To overcome this problem, color perception is described by three independent and objective variables shown in the Munsell color system: value, hue, and chroma (Figure 3-4).



• **Figure 3-4** The Munsell three-dimensional (3-D) color space. Yellow arrows show the three variables of color: value, hue, and chroma. Value increases from black to white, chroma increases from the center radially outward, and changes in hue occur in a circumferential direction. Blue arrows show the three coordinates of CIE $L^*a^*b^*$ axis: L^* (value), a^* (red-green), and b^* (yellow-blue).



• **Figure 3-5** Munsell scale of hues, values, and chromas in the color space. (From Sakaguchi RL, Powers JM: *Craig's Restorative Dental Materials*, ed 13, St. Louis, 2012, Mosby.)

Value is also known as the *gray scale* and is the vertical, or *z*-axis, on Figure 3-4. Value increases toward the high end (lighter) and decreases toward the low end (darker). Value is also expressed by the “lightness” factor, with varying levels of gray between the extremes of white and black. Teeth and other objects can be separated into lighter shades (higher value) and darker shades (lower value). For example, the yellow of a lemon is lighter than the red of a cherry. For a light-diffusing and light-reflecting object such as a tooth or dental crown, the value identifies the lightness or darkness of a color, which can be measured independently of the hue and chroma.

Hue is the dominant color of an object, for example, red, green, or blue. This refers to the dominant wavelengths present in the spectral distribution. The continuum of these hues creates the three-dimensional (3-D) color solid shown in Figure 3-4.

Chroma is the degree of saturation of a particular hue. For example, red can vary from “scarlet” to light pink, where scarlet has a high saturation and pink has a low saturation. The yellow color of a lemon is a more saturated, “vivid,” color than that of a banana, which is a less saturated, “dull” yellow. Chroma varies radially, perpendicular to the value axis (Figure 3-4). Colors in the center are dull (gray). In other words, the higher the chroma, the more intense the color. Chroma is not considered separately in dentistry and is always associated with the hue and value of dental tissues, restorations, and prostheses. The components of a color space can be more easily visualized by the individual parts in Figure 3-5, here seen as discs stacked along the value axis on a scale of 0 to 10 from black to white. Around the periphery are 10 basic hues (dominant wavelength/color). Chroma radiates out from the value axis like the spokes of a wheel.

The color space can also be quantified by the CIE (Commission Internationale de l’Eclairage) $L^*a^*b^*$ color space, in which L^* represents the value of an object from darker to

lighter, a^* is the measurement along the red ($+a^*$)-green ($-a^*$) axis, and b^* is the measurement along the yellow ($+b^*$)-blue ($-b^*$) axis (Figure 3-4).

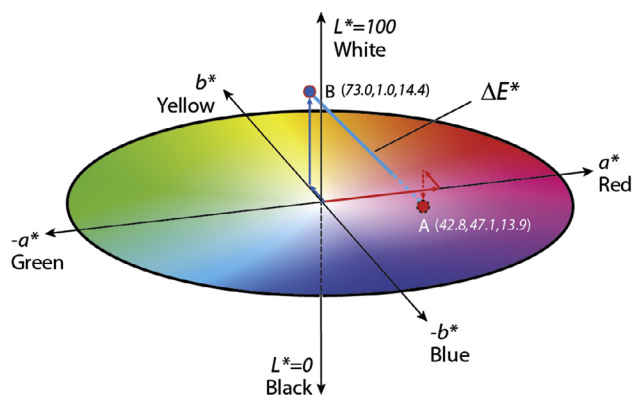
Figure 3-6 represents a horizontal plane, perpendicular to the L^* axis, through a CIE $L^*a^*b^*$ color space. The dot above the letter A is the color of a red apple, which is expressed by $L^* = 42.8$, $a^* = 47.1$, and $b^* = 13.9$. In comparison, the dot next to the letter B is for a dental body (gingival) porcelain of shade A2 with a higher (lighter) L^* of 73.0, a lower a^* of 1.0, and a higher b^* of 14.4.

In the CIE $L^*a^*b^*$ color space, the difference between two colors (ΔE^* or ΔE^*_{ab}) would be the distance between the two points representing the two colors and can be determined by the following formula:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}.$$

(1)

The color difference formula is designed to provide a quantitative representation of the color difference between a pair of colored specimens under a given set of experimental conditions. The value, however, is of little clinical significance without an understanding of the magnitude of color difference considered perceptible or acceptable by observers. The smallest perceptible color difference or *perceptibility threshold* (PT) refers to the smallest color difference that can be detected by 50% of observers under standardized conditions. The range of PT values reported in the literature is 0.4 to 4.0, with $\Delta E^* = 1.0$ being the value reported most often. Similarly, the difference in color that is esthetically acceptable by 50% of observers is known as the *acceptability threshold* (AT). The range of AT values reported in the literature is 2.0 to 6.8, with a range of 3.3 to 3.7 being the value reported most often. International Standards Organization (ISO) 28642:2016 uses a PT of $\Delta E^* = 1.2$



• **Figure 3-6** Hunter $L^*a^*b^*$ color chart. The dot above the letter A is the color of a red apple, which is expressed by $L^* = 42.8$, $a^* = 47.1$, and $b^* = 13.9$. (Courtesy Minolta Corporation, Instrument Systems Division, Ramsey, NJ.)



• **Figure 3-7** Tab arrangements of the Vitapan classical shade guide: classical group division according to hue (top row), arrangement according to value scale with no group division from lightest to darkest (middle row), and alternative arrangement according to color difference (ΔE^*) in relation to the lightest tab (bottom row). (From Paravina RD, Powers JM: *Esthetic color training in dentistry*, St. Louis, 2004, Mosby.)

and an AT of $\Delta E^* = 2.7$, established in a prospective multicenter research project.

Color Matching

In dental practice, color matching is most often performed with the use of a shade guide, such as the one shown in Figure 3-7, to select the color of ceramic veneers, inlays, or crowns. Shade-guide tabs are used in much the same way as paint chips to match the color of house paint. The individual shade tabs shown in the top row of Figure 3-7 are grouped according to hue (A, B, C, and D, where A = red-brown, B = red-yellow, C = gray, D = red-gray), followed by value (1 to 4, or lightest to darkest). This arrangement follows the “classical” order originated by Vita for porcelain. Recently, however, the trend is to arrange shade guides in decreasing order of value (lightest to darkest: B1, A1, B2, D2, A2, C1, C2, D4, A3, D3, B3, A3.5, B4, C3, A4, C4), as shown in the middle row of Figure 3-7. Matching of tooth shades is simplified by the arrangement of tabs by value; this arrange-



• **Figure 3-8** Vita shade guide used to match the restorative shade to the adjacent teeth. (Courtesy Dr. Monica Fernandez.)

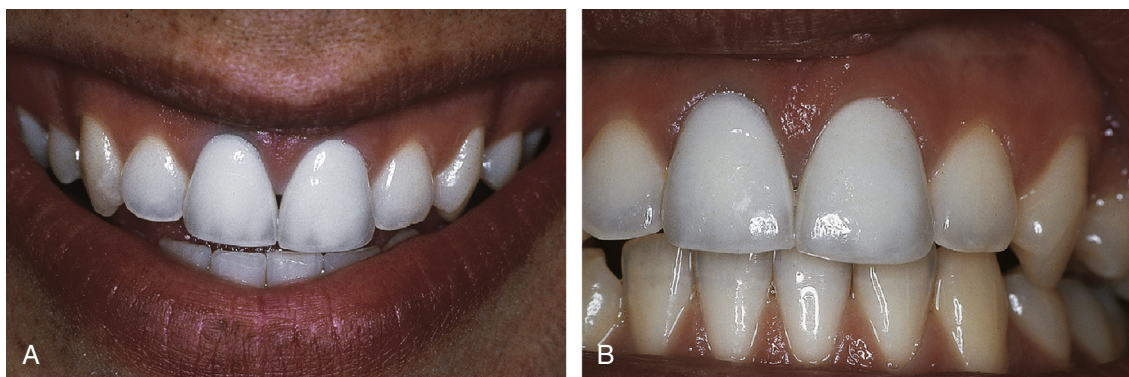
ment has been found to be easier and more reliable to use. The bottom row of Figure 3-7 shows the arrangement according to the color difference as calculated by equation (1), with respect to the lightest tab. Although a reasonable match can be achieved clinically between a tooth (or restoration) and one of the shade-guide tabs, relaying the information to a lab or technician can prove to be a challenge. To ensure esthetic results, additional information, such as drawings, descriptions, and photographs (Figure 3-8), should also be sent. Obviously, if the technician can see the actual teeth, the probability of achieving an acceptable color match will be even greater.

Further, the subjective preference of the patient must be considered. An exact match between a crown or bridge and the remaining sound teeth is not always sufficient. Patients usually prefer a lighter shade (higher value) in a restoration compared with the color of the natural teeth. Figure 3-9, A, shows the result of shade matching in which the two central incisor crowns were selected to be somewhat higher in value than the lateral incisors. Even though there is a slight mismatch, the color difference is perceptible only under close observation (Figure 3-9, B), and the patient was quite satisfied with the overall effect.

The Effect of the Observer

Signals of color are sent to the human brain from three sets of receptors in the retina called *cones*, which are especially sensitive to red, blue, and green. Factors that interfere with the true perception of color generally include low or high light levels, fatigue of the color receptors, sex, age, memory, and cultural background. However, according to a 1995 study by Anusavice and Barrett, there appears to be no effect related to observer age, gender, or clinical experience relative to the accuracy of dental shade matching.

At low light levels, the rods in the retina of the human eye are more dominant than the cones, and color perception is lost. As the brightness becomes more intense, color appears to change (Bezold–Brücke effect). Also, if an observer looks at a red object for a reasonably long time, receptor fatigue causes a green hue to be seen when he or she then looks at a white background. For this reason, if a patient is observed against an intense-colored background, the clinician may select a tooth shade with a hue that is shifted somewhat toward the complementary color of the background color. For example, a blue background shifts the color selection toward yellow, and an orange background shifts



• **Figure 3-9** Two central incisor metal-ceramic crowns with porcelain margins. **A**, The value (L^*) of these crowns is higher than that of the adjacent lateral incisor teeth. **B**, Close-up view of the crowns on the left.

the color selection toward blue-green. Unfortunately, 8% of the male and 0.5% of the female population exhibit color blindness. Most commonly, these people cannot distinguish red from green because of the lack of either green-sensitive or red-sensitive cones. However, this deficiency may not affect the shade selection of natural teeth.

The ranges of hue, chroma, and value ordinarily found in human teeth represent only a small portion of the standard color space. For example, compare Figure 3-4 within the subset of the color space shown in Figure 3-6. The selectivity of the human eye is such that accurate color matching is difficult even when one is using a shade guide that contains only a small number of shades (Figure 3-7). Recent developments in the use of digital technology for color matching are discussed in Chapter 15, Color Matching.

CRITICAL QUESTION

Why are some objects color matched under one type of illumination but mismatched under another illumination source?

The Effect of the Light Source

Because the spectral distribution of the light reflected from or transmitted through an object is dependent on the spectral content of the incident light, the appearance of an object is dependent on the nature of the light in which the object is viewed. Daylight, incandescent, and fluorescent lamps are common sources of light in the dental operator or laboratory, and each of these has a different spectral distribution. Objects that appear to be color matched under one type of light may appear different under another type. This phenomenon is called **metamerism**. Thus, if possible, color matching should be done under two or more different light sources, one of which should be daylight, and the laboratory shade-matching procedures should be performed under the same lighting conditions.

CRITICAL QUESTION

Why do some tooth-colored restorations appear to be missing when viewed under “blacklight” illumination, such as that used in nightclubs and at rock concerts?

Fluorescence

In addition to the processes already discussed, natural tooth structure absorbs light at wavelengths too short to be visible to the human eye. These wavelengths between 300 and 400 nm

are referred to as *near-ultraviolet radiation*. Natural sunlight, photoflash lamps, certain types of vapor lamps, and ultraviolet lights used in decorative lighting (“blacklights”) are sources containing substantial amounts of near-ultraviolet radiation. The energy that the tooth absorbs is converted into light with longer wavelengths, in which case the tooth actually becomes a light source. This phenomenon is called *fluorescence*. The emitted light, a blue-white color, is primarily in the 400- to 450-nm range. Fluorescence makes a definite contribution to the brightness and vital appearance of a human tooth. As an example, ceramic crowns or composite restorations that lack a fluorescing agent appear as missing teeth when viewed under a black light.

Radiopacity

X-rays, a form of electromagnetic radiation, lie at the high-energy end of the spectrum. Hence the interaction of dental biomaterials with x-radiation may be classified as an optical property. There are numerous circumstances where the ability to distinguish a dental material radiographically from the surrounding tissue is necessary. For example, sufficient radiographic contrast is required in an x-ray image to assess restorations for marginal defects or breakdown, help differentiate composite restorations from dental caries, and detect microleakage. In case of accidental ingestion or traumatic impaction of dentures or other appliances, a delay in the detection, location, and removal of the appliance and appliance fragments may be life threatening. A significant number of foreign bodies of dental origin, with many injuries and deaths, are reported each year, particularly among the elderly.

The amount of x-ray energy absorbed by an object depends on the density and thickness of the material and the energy of the radiation. Generally, the higher the atomic number of the component atoms, the greater the x-ray absorbance and the larger the contrast produced. Polymers and resins are inherently radiolucent, whereas metals with atomic numbers above about 19 (potassium) are inherently radiopaque. To impart radiopacity, restorative resins often use strontium- or barium-containing glass reinforcing particles (see Chapter 5, Imparting Radiopacity); denture polymers may (but rarely) contain barium-sulfate or other heavy-metal compound additives to render them radiopaque. Radiopacity similar to that of hard tissue provides the optimal contrast for dental restorations. When radiopacity is too low, the resin will not be visible on an x-ray image; when radiopacity is too high, this may block out and obscure details of the adjacent anatomy. Dentin has approximately the same radiodensity as that of aluminum, whereas enamel has

approximately twice the radiodensity of dentin and aluminum. To claim that a composite is radiopaque, the American Dental Association requires commercial dental restorative resins to have a radiopacity at least equal to that of aluminum. To be adequately detectable on medical chest x-ray images, a denture resin fragment of 2 mm should have a radiopacity equal to or greater than that of 0.2 mm of copper. This requires the resin to have sufficient additive to produce a radiopacity about three times that of aluminum.

Thermal Properties

When restorative materials are placed in deep cavities, the heat transmitted to vital dental pulp must be limited so as to prevent thermal shock and trauma. In other circumstances, as with denture bases in contact with mucosal surfaces, the transmission of a certain amount of thermal energy is desirable to convey the sensations of heat and cold associated with food and beverages. Such attributes are governed by the properties of thermal conductivity and thermal diffusivity. Another category of thermal behavior is the expansion when heated and contraction when cooled. If, for example, a dental restoration expands and contracts at a rate different from that of the adjacent hard tissues, marginal failures and leakage can result. This attribute is governed by the coefficient of thermal expansion.

Thermal Conductivity

Thermal conductivity (κ) is the physical property that governs heat transfer through a material by conductive flow. The conduction of heat within a solid involves the transfer of thermal energy from one end of a material to another across a temperature gradient. *Thermal conductivity* is defined as the quantity of heat in calories per second passing through a material 1 cm thick with a cross section of 1 cm² having a temperature difference of 1 **kelvin (K)** (=1 °C) and is measured under steady-state conditions in which the temperature gradient does not change. The International System (SI) unit or measure for thermal conductivity is watts per meter per kelvin ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$). In general, thermal conductivities increase in the following order, although there are exceptions: polymers < ceramics < metals.

Materials that have a high thermal conductivity are called *conductors*, whereas materials of low thermal conductivity are called *insulators*. The higher is a substance's thermal conductivity, the greater is the ability to transmit thermal energy, and vice versa. If the thermal gradient does not change (i.e., heat is supplied at one end and withdrawn at the other end at a steady rate), the thermal conductivity is a measure of the heat transferred.

CRITICAL QUESTION

What is the difference between thermal conductivity and thermal diffusivity, and why does it matter in dentistry?

Thermal Diffusivity

Thermal diffusivity (h) is a measure of the speed with which a temperature change will spread through an object when one surface is heated. Thermal diffusivity is calculated from the thermal conductivity divided by the product of density and heat capacity:

$$h = \frac{\kappa}{c_p \times \rho}, \quad (2)$$

TABLE 3-1 Density and Thermal Properties of Water, Enamel, Dentin, and Dental Materials

Material	Density (g cm ⁻³)	Specific Heat (cal g ⁻¹ K ⁻¹)	Thermal Conductivity (W m ⁻¹ K ⁻¹)	Thermal Diffusivity (cm ² s ⁻¹)
Water	1.00	1.00	0.44	0.0014
Dentin	2.14	0.30	0.57	0.0018–0.0026
Glass ionomer	2.13	0.27	0.51–0.72	0.0022
Zinc phosphate	2.59	0.12	1.05	0.0030
Composite	1.6–2.4	0.20	1.09–1.37	0.0019–0.0073
Enamel	2.97	0.18	0.93	0.0047
Amalgam	11.6	0.005	22.6	0.96
Pure gold	19.3	0.03	297	1.18

where h is thermal diffusivity, κ is thermal conductivity, c_p is heat capacity at constant pressure, and ρ is the temperature-dependent density in grams per cm³ (c_p is numerically equal to the more commonly used term *specific heat*, which is the quantity of heat needed to raise the temperature of a unit mass by 1 K).

A material with a high density and high specific heat will likely have a low thermal diffusivity. Such a material changes temperature very slowly. Low heat capacity and high thermal conductivity lead to high diffusivity, and temperature changes transmit rapidly through the material. As shown in Table 3-1, gold has about one-tenth the heat capacity of dentin, about 500 times the thermal conductivity, and about 600 times the thermal diffusivity. Thus a pure gold filling would provide the tooth pulp with very little protection against thermal shock compared with natural dentin. The thermal conductivities and thermal diffusivities of cementing materials (glass ionomer, zinc phosphate, and composite) compare favorably with enamel and dentin, in contrast with the markedly higher values for metallic restorative materials. Thus, when the remaining dentin between the cavity and the pulp is too thin to provide sufficient thermal protection, an additional layer of an insulating base material, such as the dental cements discussed in Chapter 7, *Pulp Protection*, should be placed.

During ingestion of hot foods and liquids, the thermal diffusivity reflects the thermal energy retained by the dental restorative material, whereas the thermal conductivity dictates how much thermal energy passes through this material. Because the rapid temperature changes last a short duration, the thermal energy passed could be negligible, whereas the energy retained by the material keeps the material at a higher temperature after the hot food has passed. Therefore thermal diffusivity plays a more important role than thermal conductivity clinically.

Coefficient of Thermal Expansion

When materials undergo a temperature increase, the vibrational motion of atoms and mean interatomic (bond) distances increase. This results in an increase in volume or an expansion of the material. The increase is described by the **coefficient of thermal expansion**, α , which is defined as the change in length per unit of the original length of a material when the temperature of this material

TABLE 3-2 Coefficients of Thermal Expansion (α) of Dental Materials Compared With Those of Tooth Enamel and Dentin

Material	α (ppm K ⁻¹)	α material/ α tooth enamel
Aluminous porcelain	6.6	0.58
Dentin	8.3	0.75
Commercially pure titanium	8.5	0.77
Type II glass ionomer	11.0	0.96
Tooth enamel	11.4	1.00
Gold-palladium alloy	13.5	1.18
Gold (pure)	14.0	1.23
Palladium-silver alloy	14.8	1.30
Amalgam	25.0	2.19
Dental composite	14–50	1.2–4.4
Denture resin	81.0	7.11
Pit and fissure sealant	85.0	7.46
Inlay wax	400.0	35.1

is raised 1 K (see the discussion of thermal energy in [Chapter 2, Influence of Interatomic Bond](#)):

$$\alpha = \frac{\Delta L}{L \times \Delta T}, \quad (3)$$

where L is the original length, ΔL is the change in length, and ΔT is the temperature change. Values for α of some materials of interest in dentistry are presented in [Table 3-2](#). The units are typically expressed as either mm/m/K or ppm/K.

This parameter is extremely important in dental applications as broad ranging as producing cast restorations that fit and maintaining the seal of a restoration margin. The influence of this property often dictates the procedures that have been developed for using wax patterns, casting metal crowns, placing amalgam and composite resin restorations, and preparing metal-ceramic crowns and bridges. A tooth restoration may expand or contract more than the tooth during a change in temperature; thus there may be marginal microleakage adjacent to the restoration, or the restoration may debond from the tooth. According to the values in [Table 3-2](#), direct restorative materials may experience changes in dimension of up to 4.4 times those of tooth enamel for every degree of temperature change.

The high thermal expansion coefficient of inlay wax is also important because wax is highly susceptible to temperature changes. For example, an accurate wax pattern that fits a prepared tooth contracts significantly when the wax pattern is removed from the tooth or a die in a warmer area, and then stored in a cooler area. This dimensional change is transferred to a cast metal restoration that is made by the lost wax process. Similarly, denture teeth that have been set in denture base wax in a relatively warm laboratory may shift appreciably in their simulated intraoral positions after the denture base is moved to a cooler room before processing of the denture.

Thermal stresses produced from thermal expansion or contraction differences are also important in the production of metal-ceramic

restorations. Consider a porcelain veneer that is fired to a metal substrate (coping). The veneer may contract to a greater extent than the metal during cooling and induce tangential tensile stresses or tensile hoop (circumferential) tensile stresses in the porcelain, which may cause immediate or delayed crack formation. Although these thermal stresses cannot be eliminated completely, they can be reduced appreciably by the selection of materials whose expansion or contraction coefficients are matched fairly closely (within 4%). This is discussed more fully in [Chapter 10, Bonding Porcelain to Metal](#), on ceramics.

CRITICAL QUESTION

Which factors in the oral environment promote the corrosion of metallic dental restorations and prostheses?

Electrochemical Properties

Metals undergo chemical reactions with nonmetallic elements in the environment to produce chemical compounds. This process is known as *corrosion*, which in most cases causes deterioration of the metal surface. Dentistry uses a wide variety of metals for restorations and prosthetic devices; successful clinical performance and long-term durability require adequate corrosion resistance of these materials in the oral environment. Many of the most commonly used metals derive little or no protection from the corrosion products that form under normal circumstances, which is unfortunate. The rusting of iron is a familiar example of the effects that may be produced by such a process. Gold and platinum group metals, which include ruthenium, rhodium, palladium, osmium, iridium, and platinum, resist chemical attack of this nature very well and are therefore called *noble metals*. Gold, palladium, and platinum are commonly used as dental alloys.

The oral environment is highly conducive to electrochemical action. This environment is warm, moist, and subjected to wide fluctuations in temperature and pH. Thus an understanding of corrosion and the underlying electrochemical properties is essential to control electrochemical effects and thereby minimize corrosion and corrosion-induced problems in dentistry.

Tarnish and Corrosion

A differentiation should be made between tarnish and corrosion. Even though there is a definite technical difference, clinically distinguishing between the two phenomena is difficult, and the terms are often used interchangeably in the dental literature.

Tarnish is a surface discoloration on a metal or a slight loss or alteration of the surface finish or luster. In the oral environment, tarnish often occurs from the formation of deposits or thin films, such as oxides, sulfides, or chlorides, on the surface of a restoration. Tarnish is often an early indication and precursor of corrosion. For example, eggs and certain other foods contain significant amounts of sulfur. Various sulfides, such as hydrogen or ammonium sulfide, initiate tarnish and eventually corrode silver, copper, tin, mercury, and other metals present in their alloys.

Corrosion is a process whereby deterioration of a metal is caused by a reaction with the environment. In due course, corrosion can cause severe and catastrophic disintegration of metals. Even if highly localized, corrosion may cause mechanical failure of a structure, the actual volume of material lost is quite small. Corrosive disintegration can take place through exposure to atmosphere or immersion in acid, alkaline, or certain chemical solutions. Keep in mind that saliva is an electrolyte, which is conducive to the corrosion of metallic restorations.

Classifications of Corrosion

There are two general classifications of corrosion reactions: *chemical corrosion* and *electrochemical corrosion*. In chemical corrosion, there is a direct combination of metallic and nonmetallic elements. Corrosion occurs because the most commonly used metals and alloys are not in their lowest-energy state (thermodynamically the most stable state). For example, iron (Fe) is extracted from various iron oxides. Similarly, aluminum is extracted from aluminum oxide (Al_2O_3), and copper from copper sulfide (CuS). Oxidized compounds such as Fe_3O_4 , Al_2O_3 , and CuS are thermodynamically stable and consequently occur in nature in these fully reacted forms. Thus pure metals spontaneously convert from a highly reactive state to their lowest-energy oxidized state by reacting with oxygen, sulfur, or chlorine. Another good example is the discoloration of silver by sulfur. Such a reaction is also referred to as “dry” corrosion because this reaction occurs in the absence of water or other fluid electrolytes. Notice that metals lose electrons in the corrosion process. Ceramics do not corrode by the loss of electrons because they are already fully oxidized and are in their lowest-energy states. However, the glass phase of ceramics can dissolve in acidic and basic media. Noble metals are unique; they do not form stable oxides at room temperature.

Electrochemical corrosion, also known as **galvanic corrosion**, requires the presence of water or some other fluid electrolyte and a pathway for the transport of electrons (i.e., an electrical current). This type of corrosion is also referred to as *wet corrosion* because a fluid electrolyte is required. Electrochemical corrosion is seldom isolated and almost invariably accompanied by chemical corrosion. However, the electrochemical mode of corrosion is more important for dental materials and is the focus in this chapter.

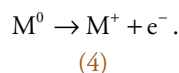
CRITICAL QUESTION

Which mechanisms of electrochemical corrosion are possible for metallic dental restorations and prostheses?

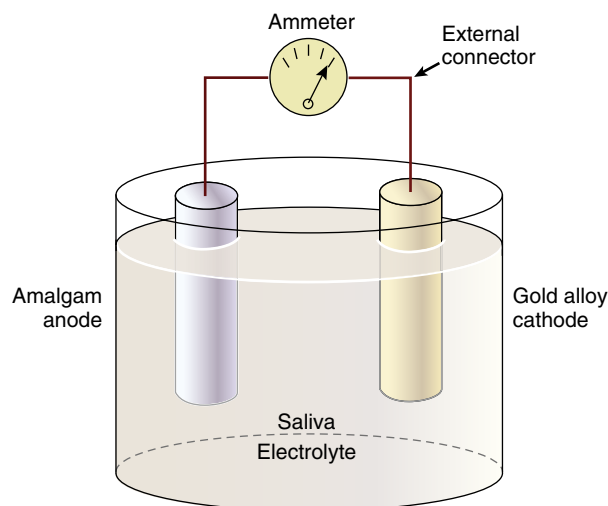
Electrochemical Mechanism of Corrosion

When a metal is immersed in a fluid electrolyte, the chemical potential causes enough ions to dissolve to form a saturated solution and produce an equal number of free electrons. The loss of electrons by a metal is known as *oxidation* and is the initial electrochemical event in the corrosion process. The ease with which a metal gives up electrons in solution and oxidizes can be expressed in terms of the *oxidation potential*. When a second metal of different composition is placed in the same solution, the second metal will then compete with the first metal to dissolve in the solution. If the two metals are connected with an external circuit, they form an electrochemical cell, as illustrated schematically in Figure 3-10.

The metal having a greater oxidation potential than the other metal will be the one that releases positive ions (M^+) with the production of free electrons, as illustrated by the following anodic/oxidation reaction:

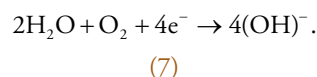
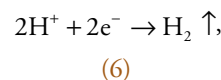
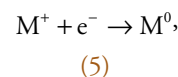


This metal is also called an *anode*, indicating the metal surface is undergoing an oxidation reaction and is corroding. Once the solution is saturated with metal ions from anode, reduction reactions occur at the other metal surface, which is called a *cathode*, where the free



• **Figure 3-10** Diagram of an electrochemical cell consisting of a simulated amalgam anode, a gold alloy cathode, and saliva as the electrolyte.

electrons produced from the anode are consumed and metal ions from the saturated solution are deposited. For example, metal ions may be removed from the solution to form metal atoms (reaction 4), as occurs in metal plating; hydrogen ions may be converted to hydrogen gas (reaction 5); or hydroxyl ions may be formed (reaction 6):



In summary, an electrochemical cell is composed of four essential components: an anode, a cathode, an external circuit, and an electrolyte. Both the anode and cathode are called *electrodes*. The electrolyte supplies the ions needed at the cathode by dissolving metal ions at the anode. The external circuit serves as a conduction path to carry electrons from the anode to the cathode because there is a difference in electrical potential that can be measured, which is known as *voltage* (V). This simple electrolytic cell is, in principle, a battery because the flow of electrons in the external circuit is capable of lighting a light bulb in a flashlight or producing a physiological sensation (i.e., pain).

In order for electrochemical corrosion to be an ongoing process, the production of electrons by the oxidation reactions at the anode must be exactly balanced by the consumption of electrons in the reduction reactions at the cathode. Often the cathodic reactions are considered to be the primary driving force for electrochemical corrosion. We will find in later discussions that keeping a reaction from happening at the cathode is recommended to reduce or eliminate corrosion.

Different metals have different tendencies for oxidation because of their differences in electronic structure; this tendency to oxidize (ionize) is measured by the *electrode potential*, expressed in volts or millivolts. To measure the electrode potential of any material is to determine the voltage difference between the metal and a standard hydrogen electrode in water at 25 °C. The potential of hydrogen electrode is arbitrarily designated as zero potential; therefore the

TABLE 3-3 Electromotive Series of the Metals

Metal	Ion	Electrode Potential (V)
Gold	Au ⁺	+1.50
Gold	Au ³⁺	+1.36
Platinum	Pt ²⁺	+0.86
Palladium	Pd ²⁺	+0.82
Mercury	Hg ²⁺	+0.80
Silver	Ag ⁺	+0.80
Copper	Cu ⁺	+0.47
Bismuth	Bi ³⁺	+0.23
Antimony	Sb ³⁺	+0.10
Hydrogen	H ⁺	-0.00
Lead	Pb ²⁺	-0.12
Tin	Sn ²⁺	-0.14
Nickel	Ni ²⁺	-0.23
Cadmium	Cd ²⁺	-0.40
Iron	Fe ²⁺	-0.44
Chromium	Cr ²⁺	-0.56
Zinc	Zn ²⁺	-0.76
Aluminum	Al ³⁺	-1.70
Sodium	Na ⁺	-2.71
Calcium	Ca ²⁺	-2.87
Potassium	K ⁺	-2.92

voltage difference measured is the electrode potential of the metal being measured. Similar measurements for the elements that are useful to the dentist yields the values that are arranged by their equilibrium values of electrode potential in Table 3-3, which is known as the **electromotive** (or *galvanic*) **series**. The sign of the electrode potential in Table 3-3 indicates the polarity in such a cell. Elements with a higher positive value have a lower tendency to dissolve and are therefore more resistant to becoming oxidized and corroded in aqueous environments. The more negative the electrode potential, the easier it is for any particular metal to ionize and oxidize and the more susceptible it is to tarnish and corrosion.

If two pure metals are immersed in an electrolyte and connected by an electrical conductor to form a galvanic cell, the metal with the more negative electrode potential in Table 3-3 becomes the anode and undergoes oxidation; that is, the ions of this metal go into solution. As an example, in a galvanic cell composed of copper (-0.46 V) and zinc (-0.76 V) electrodes in an aqueous acidic solution, the zinc electrode becomes the anode and undergoes surface dissolution.

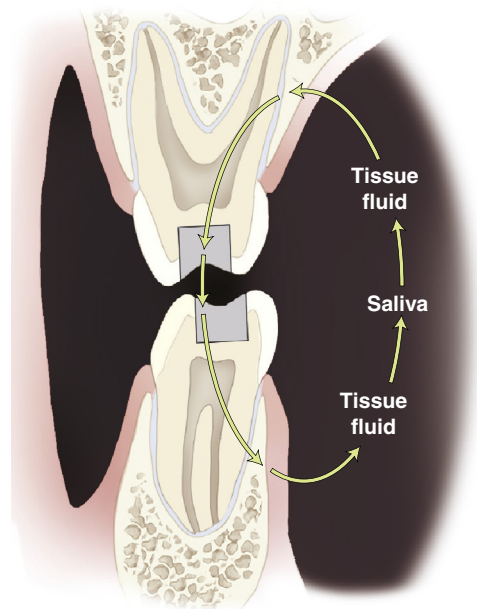
In general, the relative position of any element in the electromotive series depends not only on this element's inherent dissolution tendencies but also on the ionic concentration in the electrolyte. As the ionic concentration increases, the tendency for that element to dissolve decreases. Thus an increase in metal ion content may eventually prevent further corrosion because the metal's ions have saturated the

immediate environment. However, this would be unusual for metallic dental materials because dissolved ions are continually removed by food, fluids, and tooth brushing. Thus corrosion in the mouth is typically an ongoing process. Many types of electrochemical corrosion are possible in the oral environment because saliva, with the salts it contains, is a weak electrolyte. The electrochemical properties of saliva depend on the concentrations of components, pH, surface tension, and buffering capacity. Each of these factors may influence the strength of any electrolyte. Thus the magnitude of the resulting corrosion process will be controlled by these variables.

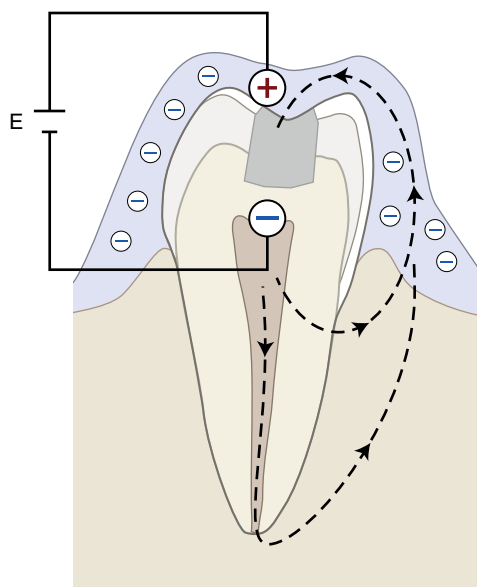
In an environment in which a metal is corroding, both anodic and cathodic reactions take place simultaneously on the surface of the metal. Metal ions go into solution because of the anodic reactions, and other ions are reduced in the cathodic reactions. These two reactions may occur at randomly distributed sites on the metal surface, or more frequently, there are anodic areas at which mostly the metal dissolves and cathodic areas at which mostly other ions are discharged. Several forms of electrochemical corrosion discussed next are based on the mechanisms that produce these inhomogeneous areas.

Dissimilar Metals

An important type of electrochemical reaction occurs when combinations of dissimilar metals are in direct physical contact. Here, the dental reference is two adjacent metal restorations where the metal surfaces are chemically dissimilar. The alloy combinations that may produce galvanic corrosion or electrogalvanism through the flow of galvanic currents may be in either continuous or intermittent contact. An example would be a dental amalgam restoration placed on the occlusal surface of a tooth directly opposing a gold inlay. Because both restorations are wet with saliva, an electrical circuit exists with a difference in potential between the dissimilar restorations (Figure 3-11). When the two restorations are brought into contact, there is a sudden short-circuit through the two alloys. This can result in a sharp pain, called **galvanic shock**, which is well known in dentistry. An undetected piece of aluminum foil in a baked potato can produce the same effect with a metallic restoration during chewing.



• **Figure 3-11** Possible path of a galvanic current in the mouth.



• **Figure 3-12** Schematic illustration of a single metallic restoration showing two possible current pathways between an external surface exposed to saliva and an interior surface exposed to dentinal fluid. Because the dentinal fluid contains a higher Cl^- concentration than saliva, it is assumed that the electrode potential of the interior surface exposed to dentinal fluid is more active; it is therefore given a negative sign (-). The potential difference between the two surfaces is represented by E.

A current is present even in a single isolated metallic restoration, although this is less intense. In this situation, the electrochemical cell is generated as a result of the electrical potential differences created by the two electrolytes: saliva and tissue fluids. The term *tissue fluid* is used to denote the dentinal fluid, soft tissue fluid, and blood that provide the means for completing the external circuit. Because the chloride ion concentration of dentinal fluid is seven times higher than that of saliva, there is an assumption that the interior surfaces of a dental restoration exposed to dentinal fluid will have a more active electrochemical potential. Possible current pathways are diagrammed in Figure 3-12.

Heterogeneous Surface Composition

Another type of galvanic corrosion is associated with the heterogeneous composition of the surfaces of dental alloys, whose microstructures have been described in Chapter 2, *Liquid-to-Solid Transformation of Cast Metals*. Commercial dental alloys generally contain more than three elements, and they can have complex microstructures that result in even more heterogeneous surface compositions. For example, when an alloy containing a two-phase eutectic microstructural constituent is immersed in an electrolyte, the lamellae of the phase (Figure 2-18) with the more negative electrode potential are attacked, and corrosion results.

In an alloy that is a single-phase solid solution, any cored structure is less resistant to corrosion than is the homogenized solid solution because of differences in electrode potential caused by microsegregation and variations in composition between individual microstructural elements (Chapter 2, *Coring and Homogenization Heat Treatment*). Even a homogenized solid solution is susceptible to corrosion at the grain boundaries, which are anodic to the cathodic grain interiors, because atomic arrangements at the grain boundaries are less regular and have higher energies (Chapter 2, *Liquid-to-Solid Transformation of Cast Metals*). Solder joints between dental alloys also corrode

because of differences in the compositions of the alloy and solder (Chapter 9, *Joining of Dental Alloys*).

Impurities in alloys enhance corrosion, and these impurities are typically segregated at the grain boundaries, as described in Chapter 2, *Liquid-to-Solid Transformation of Cast Metals*. Mercury impurities that can inadvertently contaminate gold alloys during handling by dental personnel have electrode potentials different from those of the bulk grains of the gold alloys. Finally, it follows from the preceding discussion that nominally pure metals, which do not contain significant quantities of impurities or secondary microstructural phases acting as miniature electrodes with different potentials, corrode at much slower rates than alloys do.

Stress Corrosion

Because the imposition of stress increases the internal energy of an alloy, either through the elastic displacements of atoms or the creation of microstrain fields associated with dislocations (when permanent deformation occurs, as described in Chapter 9, *Dislocation Movement in Polycrystalline Alloys*), the tendency to undergo corrosion will be increased. For most metallic dental appliances, the deleterious effects of stress and corrosion, called **stress corrosion**, are most likely to occur during fatigue or cyclic loading in the oral environment. Thus any adjustment of the alloy by bending, burnishing, or malleting causes localized permanent deformation in some parts of the appliance. This adjustment results in the creation of electrochemical cells, which consist of the more deformed metal regions (anodic), saliva, and the not so deformed or less deformed metal regions (cathodic), wherein the deformed regions will undergo corrosion attack. This is one reason excessive burnishing of the margins of metallic restorations is contraindicated.

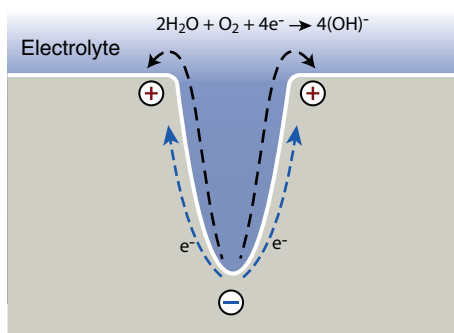
CRITICAL QUESTION

How can a small pit in the surface of a metallic restoration or a gap between a metal restoration and a tooth become susceptible to and sustain aggressive, localized corrosive attack?

Concentration Cell Corrosion

An important type of electrochemical corrosion is called **concentration cell** corrosion, which occurs whenever there are variations in the electrolytes or in the composition of the given electrolyte within the system. When surface irregularities, such as pits, scratches, and cracks, in restoration surfaces are covered with saliva, the saliva around the rim of the irregularities being exposed to the atmosphere will be richer in oxygen concentration relative to the saliva at the bottom of the irregularities. Recall reaction 7 that occurs at the cathode of an electrochemical cell where the areas around the rim are likely to become the cathode and begin to draw electrons from oxygen-poor regions, such as the bottom of the irregularities, to complete the reaction (Figure 3-13). Consequently, metal atoms at the base of the pit ionize (i.e., reaction 4) and go into solution to generate the electrons needed, causing the pit to deepen. Thus to protect against such *pitting corrosion*, all metallic dental restorative materials should be polished. A closely related category of concentration cell corrosion is “*crevice corrosion*,” in which preferential attack occurs at the crevices and marginal gaps of crowns, bridges, and cavity restorations because of the presence of food debris and other deposits.

There are often accumulations of food debris in the interproximal areas of the mouth, particularly if oral hygiene is poor. This debris then produces one type of electrolyte in that area, and the normal saliva provides another electrolyte at the occlusal surface. Therefore



• **Figure 3-13** A pit on a dental alloy as a corrosion cell. The region at the bottom of the pit is an anode, and the surface around the rim of the pit is the cathode. The metallic ions flow from the bottom to the rim through the electrolyte, and the electrons flow through the metal to the rim.

electrolytic corrosion occurs with preferential attack of the metal surface occurring underneath the layer of food debris. There is also the possibility that the region covered by the debris or plaque is oxygen-poor and becomes anodic relative to the rest of the restoration.

Seldom are any one of the preceding types of electrochemical corrosion found alone. Generally, two or more types act simultaneously, thereby compounding the problem. This phenomenon can be illustrated by considering the dissimilar metal corrosion between a cast gold inlay and an amalgam restoration. Because surface deposits can form during this type of electrochemical corrosion, differences in oxygen concentration will arise. Moreover, if the corrosion product layer is incomplete or porous, as is usually the case with metallic dental restorations, the resulting inhomogeneous surface will produce new electrochemical cells for continued corrosion. Obviously, good oral hygiene helps to prevent the accumulation of surface deposits and is thus essential for minimizing corrosion.

Protection Against Corrosion

Gold coating is employed to enhance the appearance of many commercial nondental products. However, when the gold coating becomes scratched or pitted to a depth where the substrate metal is exposed, the metal corrodes at a very rapid rate because of concentration cells and dissimilar metals in contact. Attempts to use metallic and nonmetallic coatings to provide corrosion protection for dental alloys have generally been ineffective because such coatings were too thin, incomplete, not adherent to the underlying metal, readily scratched, or attacked by oral fluids.

However, when two dissimilar metals are in contact, paint or another nonconductive film can be used to minimize corrosion if this is applied to the more noble metal between the two involved. Should a scratch occur on the protective film, the exposed cathode area is very small and can be filled quickly by the corrosion product from the anode, which effectively isolates the cathode.

A highly effective protection uses certain metals that develop a thin, adherent, highly protective film by reaction with the environment; such a metal is said to be *passive*. The most common example is stainless steel, which contains sufficient amounts of chromium added to passivate the alloy with chromium oxides. The same principle is used in dental alloys not based on noble metals, as described in [Chapter 9, Classification of Dental Casting Alloys](#). Tensile stress and certain ions, such as chlorine ions, can disrupt the protective oxide film, leading to rapid corrosion. Therefore patients should be warned against using household bleaches for cleaning partial denture frameworks or removable orthodontic appliances that are alloyed

with chromium. Titanium (Ti) also forms a passivating titanium oxide film, which is of interest because both commercially pure Ti and alloys in which Ti is a major component are used for a variety of dental applications, such as cast restorations, orthodontic wires, endodontic instruments, and implants discussed in [Chapters 9 and 12](#). Titanium and Ti alloys are widely used in dentistry because of their favorable combination of chemical, physical, and biological properties and their resistance to corrosion. Their consequent biocompatibility is among their major advantages. Nevertheless, corrosion can occur, and the long-term accumulation of corrosion products can lead to fractures of the alloy–implant interface, implant abutment, or implant body. The combination of stress, corrosion, and bacteria contributes to implant failure.

Noble metals resist corrosion because their electromotive force is positive with regard to any of the common reduction reactions found in the oral environment. To corrode a noble metal under such conditions, an external current (overpotential) is required. A guideline that has been employed by the manufacturers of many dental alloys is that at least half the atoms should be noble metals (gold, platinum, and palladium) to ensure against corrosion. Palladium has been found to be effective in reducing the susceptibility to sulfide tarnishing for alloys containing silver. If noble metals are used to avoid corrosion, it is important that the more active constituents of the alloy be uniformly dispersed in a random solid solution because the formation of a second phase that is enriched in an active metal will produce a galvanic corrosion cell.

Clinical Significance of Galvanic Currents

Small galvanic currents associated with electrogalvanism are known to be continually present in the mouth, promoting corrosion, as discussed earlier. As long as metallic restorative materials are employed, the elimination of these galvanic currents is unlikely. Although post-operative pain caused by galvanic shock is not common, this can be a source of discomfort to an occasional patient. However, such post-operative pain usually occurs immediately after the insertion of a new restoration and generally subsides and disappears in a few days. The primary factor responsible for the pain resulting from this current flow is likely the physiological condition of the tooth. Once the tooth has recovered from the injury of preparing the cavity and has returned to a more normal physiological condition, the current flow produces no response. The most practical method for reducing or eliminating galvanic shock is a varnish coating on the surface of the metallic restoration. As long as the varnish remains, the restoration is insulated from saliva, and no electrochemical cell is established. By the time the varnish has worn away, the pulp has usually healed sufficiently such that no pain persists.

The balance of evidence shows that galvanic currents are deleterious only from the standpoint of patient discomfort—and even then, only rarely. Nevertheless, dentists should avoid clinical procedures that exacerbate the condition, such as insertion of an amalgam restoration directly in contact with a gold crown. Mercury released from the corroding amalgam (the anode) may interact with the gold alloy (the cathode) and weaken the amalgam restoration. A discoloration of both restorations may also occur, and often a metallic taste develops that can persist indefinitely.

Magnetic Materials

Magnetic materials are ubiquitous, being found in a wide range of everyday items, from magnetic bulletin boards to compasses to electrical generators. In dentistry, they are primarily used for

retention of implant-borne prostheses and for orthodontic tooth movement. The force that **magnets** deliver is biologically safe and can be directed and exerted both within the mouth and through soft and hard tissues.

Magnetism occurs in nature in *magnetite*, a magnetic iron oxide, and in the synthetic alloys aluminium-nickel-cobalt (AlNiCo), platinum-cobalt (PtCo), samarium-cobalt (SmCo), and neodymium-iron-boron (NdFeB). Magnetism develops from circulating electrical currents. In magnetic materials, the circulation is caused by electrons orbiting within the atoms. In most materials the magnetic effects among the electrons cancel out, but in iron and the alloys just mentioned, a net magnetic field is induced when the atoms are properly aligned. This alignment produces a magnetic field, which emerges from one pole (north pole) and returns to the other (south) pole. A magnetic field induces changes in the surrounding medium in proportion to flux density, the unit of which is the **tesla** (T), and the flux density is proportional to the size of the magnet. Attraction or repulsion between two magnets is dependent on their pole orientation and is inversely proportional to the square of the distance between them. These properties result in a dramatic reduction in attractive or repulsive force when magnets are not optimally aligned and not in close proximity.

A major shortcoming of magnets is their susceptibility to corrosion and need to be protected by a highly durable coating. Another problem is the loss of magnetic flux over time or in the presence of elevated temperatures. In dentistry, the magnetic materials used generate a constant field that is permanent at mouth temperatures. However, heating to relatively modest temperatures can cause irreversible magnetic loss. For example, this can occur in applications where magnets are embedded in acrylic appliances that, during curing, reach temperatures of 80 °C to 90 °C from the exothermic setting reaction of the methyl-methacrylate resin (see [Chapter 11, Temperature Rise](#)).

Within their range of current dental uses, magnets and static magnetic fields have been found to be biologically safe if the flux is less than 40 mT, according to the guidelines of the International Commission on Non-Ionizing Radiation Protection and the World Health Organization. According to these organizations, vertigo and nausea are experienced when the head moves rapidly in a field greater than 2 T, as might occur during medical magnetic resonance imaging. These symptoms derive from the disturbance of vestibular function by induced current in the central nervous system. There is little evidence of other effects, including carcinogenesis, although experimental data are still sparse. Magnetic fields developed near the gingiva by magnetic attachments for removable partial dentures have been reported to be well below 40 mT—in the 10- to 15-mT range.

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Based on a study of the influence of light intensity on the ability to discriminate color differences within the color range of natural teeth. A significant number of the dentists in the study were found to be color-deficient. In such instances, the dentist should obtain assistance when matching tooth shades.
- Berzins DW, Kawashima I, Graves R, et al: Electrochemical characteristics of high-Pd alloys in relation to Pd-allergy, *Dent Mater* 16:266–273, 2000.
In vitro electrochemical evaluations of a variety of palladium-containing alloys provide insight into the mechanism of palladium allergy for some patients.
- Calamia JR, Trushkowsky RD, Wolff MS, editors: Successful esthetic and cosmetic dentistry for the modern dental practice update 2011, *Dent Clin N Am* 55:187–418, 2011.
Presents the clinical steps needed to achieve predictable esthetic color management.
- Chaturvedi TP: An overview of the corrosion aspect of dental implants (titanium and its alloys), *Indian J Dent Res* 20:91–98, 2009.
- Chrcanovic B, de Souza LN: Tracheotomy for a foreign body in the larynx, *Oral Maxillofac Surg* 13:55–58, 2009.
Shows radiograph of a swallowed partial denture. Such inadvertently swallowed foreign objects can be immediately life-threatening and must be adequately radiopaque to safely determine and direct removal.
- Goodacre CJ, Paravina RD, Bergen SE, et al: A contemporary guide to color and shade selection for prosthodontists, *American College of Prosthodontists* 2009. [Educational DVD.]
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This article describes dental alloy compositions and their properties. It discusses the safety and efficacy considerations of dental alloy devices. The article defines and compares interstitial fluid and oral fluid environments. Also, the effects of restoration contact on electrochemical parameters are examined, and the concentration of cells developed by dental alloy-environment electrochemical reactions are reviewed.
- Paravina Rade D: Dental Color Matcher/an online education and training program for esthetic dentistry. <http://www.scadent.org/news/free-color-training>.
This online CE course presents a novel approach to practical shade matching and advanced esthetics.
- Upadhyay D, Panchal MA, Dbey RS, et al: Corrosion of alloys used in dentistry: A review, *Mater Sci Eng A* 432:1–11, 2006.
- Yuan JC-C, Brewer JD, Monaco EA, et al: Defining a natural tooth color space based on a 3-dimensional shade system, *J Prosthet Dent* 98:110–119, 2007.
Not all commercial shade guides cover all the areas of value, hue, and chroma present in human tooth structure. These articles analyze and present examples of this problem.

Full Selected Readings for this chapter can be found on www.expertconsult.com.

Selected Readings (Web Version)

Physical Properties

Chrcanovic B, de Souza LN: Tracheotomy for a foreign body in the larynx, *Oral Maxillofac Surg* 13:55–58, 2009.

Shows radiograph of a swallowed partial denture. Such inadvertently swallowed foreign objects can be immediately life-threatening and must be adequately radiopaque to safely determine and direct removal.

Haidary A, Leider JS, Silbergleit R: Unsuspected swallowing of a partial denture, *Am J Neuroradiol* 28:1734–1735, 2007.

A recent case report of a swallowed partial denture lodged in the hypopharynx and upper esophagus. The subtle imaging appearance and difficulty of detection and location of the swallowed denture is discussed.

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This is a series of papers covering the many facets of selecting materials and clinical procedures used in esthetic dentistry. Depicted are the improved services available through bonding technology, with particular emphasis on the organization of color in the design and fabrication of restorative materials.

Antonson SA, Anusavice KJ: Contrast ratio of veneering and core ceramics as a function of thickness, *Int J Prosthodont* 14:316–320, 2001.

Barna GJ, Taylor JW, King GE, et al: The influence of selected light intensities on color perception within the color range of natural teeth, *J Prosthet Dent* 46:450–453, 1981.

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Calamia JR, Trushkowsky RD, Wolff MS, editors: Successful esthetic and cosmetic dentistry for the modern dental practice: Update 2011, *Dent Clin N Am* 55:187–418, 2011.

Presents the clinical steps needed to achieve predictable esthetic color management.

Chu S, Devigus A, Mieleszko A: *The Fundamentals of Color: Shade Matching and Communication in Esthetic Dentistry*, Carol Stream, IL, 2004, Quintessence.

Cleland TM: The Munsell color system. A practical description with suggestions for its use. <http://www.applepainter.com>.

An especially useful explanation of complementary colors is given in Chapter 5.

Goodacre CJ, Paravina RD, Bergen SF, et al: A contemporary guide to color and shade selection for prosthodontists, *American College of Prosthodontists*, 2009. [Educational DVD.]

McLean JW: *The science and art of ceramics. Vol. 1: The nature of dental ceramics and their clinical use*1, Amador City, CA, 1979, Quintessence.

For those interested in an in-depth discussion of principles of color as related to dental ceramics, basic fundamentals are clearly interwoven with clinical procedures.

Paravina Rade D: Dental Color Matcher/an online education and training program for esthetic dentistry. <http://www.scadent.org/news/free-color-training>.

This online CE course presents a novel approach to practical shade matching and advanced esthetics.

Parker RM: Shade matching for indirect restorations in the esthetic zone, *J Cosmet Dent* 23:98–104, 2008.

Yuan JC-C, Brewer JD, Monaco EA, et al: Defining a natural tooth color space based on a 3-dimensional shade system, *J Prosthet Dent* 98:110–119, 2007.

Not all commercial shade guides cover all the areas of value, hue, and chroma present in human tooth structure. These articles analyze and present examples of this problem.

Electrochemical Properties

Berzins DW, Kawashima I, Graves R, et al: Electrochemical characteristics of high-Pd alloys in relation to Pd-allergy, *Dent Mater* 16:266–273, 2000.

In vitro electrochemical evaluations of a variety of palladium-containing alloys provide insight into the mechanism of palladium allergy for some patients.

Chaturvedi TP: An overview of the corrosion aspect of dental implants (titanium and its alloys), *Indian J Dent Res* 20:91–98, 2009.

Marek M: Interactions between dental amalgams and the oral environment, *Adv Dent Res* 6:100–109, 1992.

A review of corrosion in dental amalgam and its physical, chemical, and biological consequences.

Megremis S, Carey CM: *Corrosion and Tarnish of Dental Alloys*, ASM Handbook, Metals Park, OH, 2006, American Society for Metals Int, pp. 891–921.

This article describes dental alloy compositions and their properties. It discusses the safety and efficacy considerations of dental alloy devices. The article defines and compares interstitial fluid and oral fluid environments. Also, the effects of restoration contact on electrochemical parameters are examined, and the concentration of cells developed by dental alloy-environment electrochemical reactions are reviewed.

Upadhyay D, Panchal MA, Dbey RS, et al: Corrosion of alloys used in dentistry: A review, *Mater Sci Eng A* 432:1–11, 2006.

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4

Mechanical Properties of Solids

OUTLINE

What Are Mechanical Properties?

Stress-Strain Properties

Other Strength Test Methods

Fracture of Restorations

Properties of Surface Interactions

Strength of Tooth Structure

Selection of Dental Materials

KEY TERMS

Brittle Relative inability of a material to deform plastically before it fractures.

Deformation Change in dimension caused by force application. If the deformation recovers when the force is removed, it is called *elastic deformation*. If deformation does not recover completely when the force is removed, the amount of deformation that does not recover is called *permanent* or *plastic deformation*.

Ductility The amount of plastic deformation a material can sustain under tension before fracture. This property is reported quantitatively as percent elongation.

Elastic limit Magnitude of elastic stress above which plastic deformation occurs.

Elastic modulus (also modulus of elasticity and Young's modulus) Resistance to elastic deformation of a material by force that is calculated as the ratio of elastic stress to elastic strain.

Fracture toughness The critical stress-intensity factor at the point of rapid crack propagation in a solid containing a crack of known shape and size.

Hardness Resistance of the surface of a material to plastic deformation, which is typically produced by forcing a pointed or spherical indenter on the surface.

Malleability Ability to be hammered or compressed plastically into thin sheets without fracture.

Pressure Force per unit area acting on the surface of a material. This is different from *stress*, which refers to the distribution of force within the material.

Proportional limit Magnitude of elastic stress below which stress remains proportional to strain on a stress-strain curve.

Resilience The amount of elastic energy per unit volume that is sustained on loading and released on unloading of a test specimen.

Strain Change in dimension per unit initial dimension. In mechanical testing, the change in length is used. There are elastic strain and plastic strain.

Strain hardening (work hardening) Increase in strength and hardness and decrease in ductility of a metal that result from plastic deformation.

Strength (1) Stress at the point the material fractures; depending on method of loading, there are tensile, compressive, shear, torsional, flexural, and impact strengths. (2) Maximum stress that a structure can withstand without sustaining a specific amount of plastic strain; this is known as *yield strength* or *proof stress*.

Stress Force per unit area within a structure subjected to a force; depending on the direction of force relative to the object, there are tensile, compressive, and shear stresses.

Stress concentration Area or point of significantly higher stress that occurs because of a structural discontinuity such as a crack or pore or a marked change in dimension.

Stress intensity (stress intensity factor) Relative increase in stress at the tip of a crack of given shape and size when the crack surfaces are displaced in the opening mode (also known as *fracture toughness*).

Toughness Ability of a material to absorb elastic energy and deform plastically before fracturing; measured as the total area under a plot of tensile stress versus strain.

Tribology The study and application of the principles of friction, wear, and lubrication.

True stress Ratio of applied force to the actual (true) cross-sectional area; however, for convenience, stress is often calculated as the ratio of applied force to the initial cross-sectional area.

Yield strength The stress at which a test specimen exhibits a specific amount of plastic strain.

We learned in [Chapter 1, Indirect Restorative Materials](#), that partially edentulous patients may receive removable partial dentures (RPDs) when the construction of a fixed bridge is not the best treatment option. You will learn later that RPDs are retained and supported by abutment teeth, to which they are attached by clasps, which are often made of alloys as the

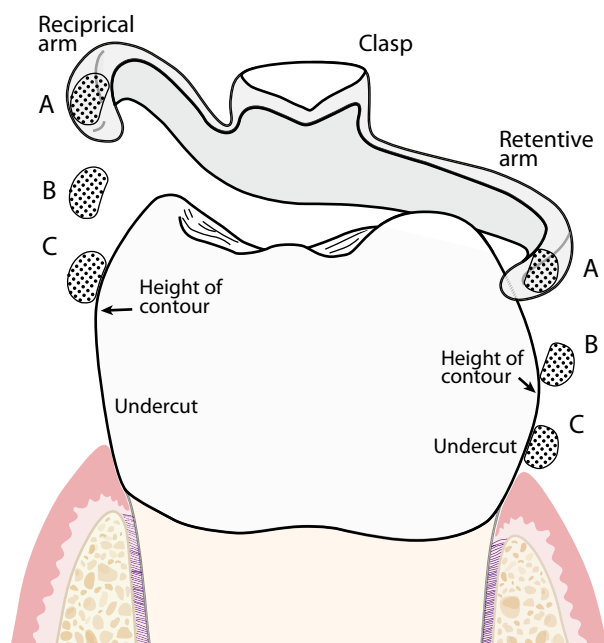
frameworks ([Figure 1-12](#)). [Figure 4-1](#) illustrates the stages of seating a clasp to an abutment tooth. The dotted patches represent the cross sections of the clasp as it is being seated. The greatest convexity or bulge, farthest from the axis of the tooth, is called the *height of contour* of the tooth. The area that is recessed relative to the height of the contour of the tooth or

recessed relative to any part of the tooth surface is known as the *undercut*. The clasp that engages an undercut area on the abutment tooth for the purpose of retention is known as a *retentive clasp*. The clasp opposite the retentive clasp, which engages the surface area occlusal to the height of contour of the tooth, is known as the *reciprocal clasp*. Greater than 180° encirclement of the abutment tooth allows for stabilization of the RPD.

During the insertion of the device, the patient positions the clasps above their respective abutment teeth (position *A* in Figure 4-1) and forces the device to seat completely, which requires the clasp to traverse. This design means that the retentive clasp arm must flex open to slide past the height of contour of the tooth (position *B* in Figure 4-1), and then flexes back to engage the undercut area (position *C* in Figure 4-1). Meanwhile, the reciprocal clasp will properly engage the tooth above the height of contour (position *C* in Figure 4-1).

After wearing the device over some period of time, the patient begins to notice that the RPD is no longer retentive and moves up and down during chewing. The dentist will recognize that most likely, the retentive clasp has lost adaptation to the tooth surface because of *deformation*, resulting from repeated insertion and removal followed by chewing on the device. For metallic clasps, the dentist will use a pair of pliers to adjust the clasp to the original position by bending. The process can be repeated whenever the device becomes loose again, but there is a limit to the number of times the clasp can be bent. Eventually, the clasp breaks during adjustment.

This sequence of events illustrates how a material responds to applied force through changes of configuration. First, the clasp flexes slightly to slide over the height of contour and returns to the initial dimension to engage the undercut. A material is an elastic solid, or is said to behave elastically, when it exhibits the ability to deform (change in configuration) under an applied force and regain the original shape and size when the force is removed. When the clasps become loose because of permanent deformation after a



• **Figure 4-1** Stages of removable partial denture (RPD) clasp seating. Dotted patches represent the cross sections of the clasp arms. The area recessed relative to the height of the contour is known as the *undercut*. *A*, Before seating. *B*, The retentive clasp passing the height of contour. *C*, Seating completed.

period of service, they are adjusted to restore their original configuration. *Plasticity* is the ability of solids to change shape permanently when subjected to forces without rupture, whereas the quantity of permanent deformation the clasp can sustain before rupture is known as *ductility*. This sequence can also be demonstrated by flexing an orthodontic wire (elastic deformation), bending the wire further to make a 90° angle (plastic deformation), and bending back and forth several times at the same bend until the wire breaks.

The focus of this chapter is to describe the mechanical characteristics of these materials and discuss the basic principles behind these mechanical properties.

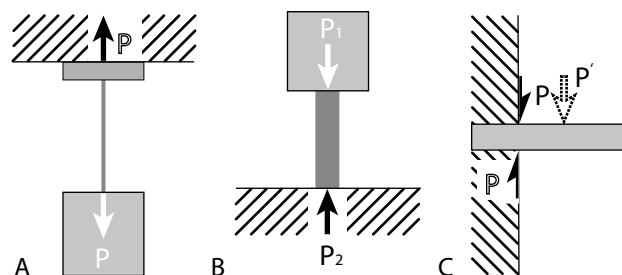
What Are Mechanical Properties?

We can perform the same exercises on a series of solid materials of any size and shape and label them as *stiff* or *flexible*, *hard* or *soft*, *brittle* or *ductile*, and *fragile* or *tough*, based on the materials' responses. A brittle material is one that fractures without exhibiting plastic deformation. These descriptions are known as *mechanical properties* because they characterize a material's resistance to elastic deformation, plastic deformation, or fracture under an applied force. However, these are qualitative terms that do not indicate how similar or dissimilar materials of the same type may be. To enable clinicians to select appropriate materials, their mechanical properties must be defined and quantified. For this purpose, the direction of force being applied, along with the magnitude of the force and the area of contact with the material, must be known. We also need to define the parameters measuring the deformation exhibited by the material and the resistance of the material to plastic deformation or fracture under a force. The parameters used for these purposes are *stress*, *strain*, and *strength*.

Stress

Force, as defined in Chapter 1, *What Is Force*, is the interaction of one object with another during actions of push or pull, and the quantity of force is measured using the unit of newton (N). Take the bending clasp as an example; our hand is one object bending the clasp (second object) to induce plastic deformation (adjustment) of the clasp. We can treat that action like we apply a force on an object. Newton's third law of motion states that when an external force acts on a solid, a reaction occurs to oppose this force, which is equal in magnitude but opposite in direction to the external force. That reaction force from the material is the resistance we feel during the interaction.

In Figure 4-2, *A*, a block of material weighing 20 kg is hung to the ceiling by a wire with a cross-sectional area of 7 mm². The



• **Figure 4-2** Illustration of simple stresses. *A*, Tensile stress. *B*, Compressive stress. *C*, Shear stress. When the load in shear test is not applied along the wall (*hollow arrow*), the test is no longer a pure shear stress but becomes a bending test.

weight stretches the wire slightly, which generates internal forces between atoms. The gravitational force exerted on the wire with a mass of 1 kg is about 9.8 N. We can reasonably assume that the distribution of the internal forces over the cross section of the wire is uniform. The stress (σ), by definition, is the exerted force per unit area perpendicular to the force direction:

$$\sigma = \frac{20 \times 9.8 \text{ N}}{7 \times 10^{-6} \text{ m}^2} = 28 \times 10^6 \text{ Pa} = 28 \text{ MPa.} \quad (1)$$

The International System (SI) unit of stress is N/m^2 and is known as a pascal (Pa). Because the unit of Pa, as defined, is very small, MPa for megapascal ($=10^6$ pascals) is customarily used. In the present example, the stress in the wire is 28 MPa in tensile mode. The weight of the wire is insignificant relative to the force applied and is usually ignored in the calculation.

When the same block is placed on a supporting post with a cross-sectional area of 140 mm^2 (Figure 4-2, B), calculation shows that the stress within the post is 1.4 MPa in compression mode. The force applied at the top of the post divided by the contact area has the same value as the stress, but this value is known as **pressure** (p) because this is the force or load that is exerted on the outer surface and not within the supporting post.

The stresses developed according to the nature of the applied forces and the object's shape are tensile, compressive, and shear stresses (Figure 4-2).

Tensile Stress

Figure 4-2, A shows the mode of tension along the long axis of a wire where a pair of forces is pulling away along the wire axially. The two forces are the weight of the block and the reaction force from the ceiling. The stress generated in the wire is tensile stress and should be the same throughout the entire wire if the cross-sectional area is uniform. You can roll up a sheet of rubber dam and generate tensile stress within the roll by pulling at both ends.

Compressive Stress

When the post is resting on a surface, there is a reaction force from the surface pushing upward (Figure 4-2, B), which illustrates the mode of compression along the long axis of the post. The stress generated within the post is known as *compressive stress*. The contact area of the supporting surface is also under compressive loading

from the post, except that the compressive stress generated within the supporting material is dispersed beyond the area of contact, laterally and vertically. The stress is higher under the area of contact and decreases with distance from the area of contact. This pattern is known as *stress distribution* or *stress gradient*. When a patient bites a bolus of food between an upper and a lower tooth, both teeth are exposed to compressive load and undergo compressive stress.

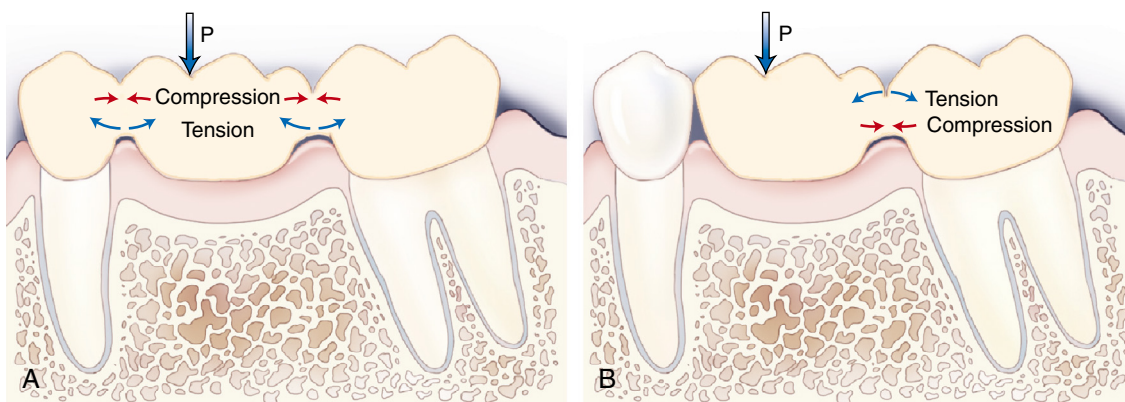
Shear Stress

When a bar is fixed at one end of a panel (Figure 4-2, C) and downward force perpendicular to the long axis of the bar is applied along the surface of the panel, there is an upward reaction force from the panel, which acts on the bottom of the bar. Note that the direction of the reaction force is opposite to that of the applied force but not along the same path. This is a characteristic of shear force. The shear stress of the section of the bar that is experiencing the shear force is divided by the cross section of the area. In orthodontic treatment, the wire delivers forces to brackets; the horizontal component of the force relative to the bonded enamel surface will generate shear stress within the bracket and within the resin bonding cement. Debonding may occur by shear-stress failure of the bonding cement. Debonding of the brackets can also be achieved by twisting the bracket with orthodontic pliers. This mode of action is called *torsion*, where the plier functions as a lever. This action is the torque that debonds the bracket. Note that the force applied through the pliers is to rotate the bracket, and the length of the pliers enhances the tendency to twist the bracket. Therefore, the tendency is not measured by force but *moment*, which is the force multiplied by the length of the pliers. Moment and torque are like forces that can cause the objects to move; the difference is that they can be amplified with the help of a longer lever.

If the downward force applied on the bar is away from the panel, the stress developed within the bar is no longer purely shear stress but also includes additional tensile and compressive stresses as the bar bends. More on this phenomenon is discussed in the section on flexure tests.

Combined Stresses

For complex objects, such as three-unit fixed dental prostheses (FDPs; Figure 4-3, A) and two-unit cantilever FDPs (Figure 4-3, B), the stresses generated in these devices are different from those in the simple objects shown in Figure 4-2. As the patient chews, the masticatory load causes the pontic to bend toward the tissue even



• **Figure 4-3** Types of stresses acting on a fixed dental prosthesis (FDP). **A**, Stresses induced in a three-unit bridge by a flexural force (P). **B**, Stresses induced in a two-unit cantilever bridge. Note that the tensile stress develops on the gingival side of the three-unit bridge and on the occlusal side of the cantilever bridge.

though the change is not visually detectable. In the three-unit FDP, the bending causes the pontic to become concave (contract slightly) and the tissue side to become convex (stretch slightly). Therefore there is compressive stress on the occlusal side and tensile stress on the tissue side. Both stresses concentrate at the connector because of the smaller cross-sectional area than that of the pontic. In the case of cantilevered FDPs, the unsupported end will bend the most, leaving the occlusal surface convex and the tissue side concave. Therefore there is tensile stress on the occlusal side and compressive stress on the tissue side. Both stresses will also concentrate at the connector area. Note that there is a moment acting on the abutment tooth in the occlusal-gingival direction that could result in failure of the cement and loosening of the prosthesis. A longer span of the FDP will place more burden on the cementing medium.

Dental restorations and devices in the oral cavity may be subjected to tension, compression, shear, torsion, or bending. The types of stresses developed within the restoration or devices would likely be a combination of tensile, compressive, and shear stresses.

Strain

Materials respond to forces through changing shape or dimension. Deformation resulting from tensile or compressive forces is one dimension that can be measured directly. The ratio of the change in length, ΔL , divided by the original length, L_0 , is the strain (ϵ) of that material under a given load. If the wire in Figure 4-2, A is 100 mm long before loading and increases by 0.5 mm ($\Delta L = 0.5$ mm) when loaded, the strain is as follows:

$$\epsilon = \frac{\Delta L}{L_0} = \frac{0.5 \text{ mm}}{100 \text{ mm}} = 0.005 = 0.5\%.$$

(2)

We can conclude that the wire reaches a stress of 28 MPa with a tensile strain of 0.5%. When the load is removed, and the length of wire recovers to 100 mm, the wire exhibits all elastic strain under the weight. If the wire does not recover completely when the load is removed and registers a length of 100.2 mm ($\Delta L = 0.2$ mm), the strain value will be 0.2%, which is the plastic strain the weight caused. The difference between the two values is 0.3%, which is the maximum elastic strain of the wire. Maximum elastic strain is also called *flexibility* and is discussed in detail later in the chapter.

When we add more weight to the wire until the breaking point, and the total length of the two broken wires is 101.3 mm ($\Delta L = 1.3$ mm), this means that the wire sustained 1.3% of plastic deformation at fracture. Keep in mind that when the wire breaks, the elastic strain vanishes because there is no stress in either piece of the wire. The value obtained is also called *elongation* or ductility. The clinical relevance of this property is discussed later in the chapter. Note that strain is a dimensionless quantity; units such as meter per meter or centimeter per centimeter are often used to remind one of the system of units employed in the actual measurement. The accepted equivalent in the English system is inch per inch, foot per foot, and so forth.

By now you should realize that whenever there is a stress applied on a material, the material should exhibit a corresponding strain. The relationship between stress and strain during the elastic deformation is the elastic property of the material and is discussed in detail in the next segment.

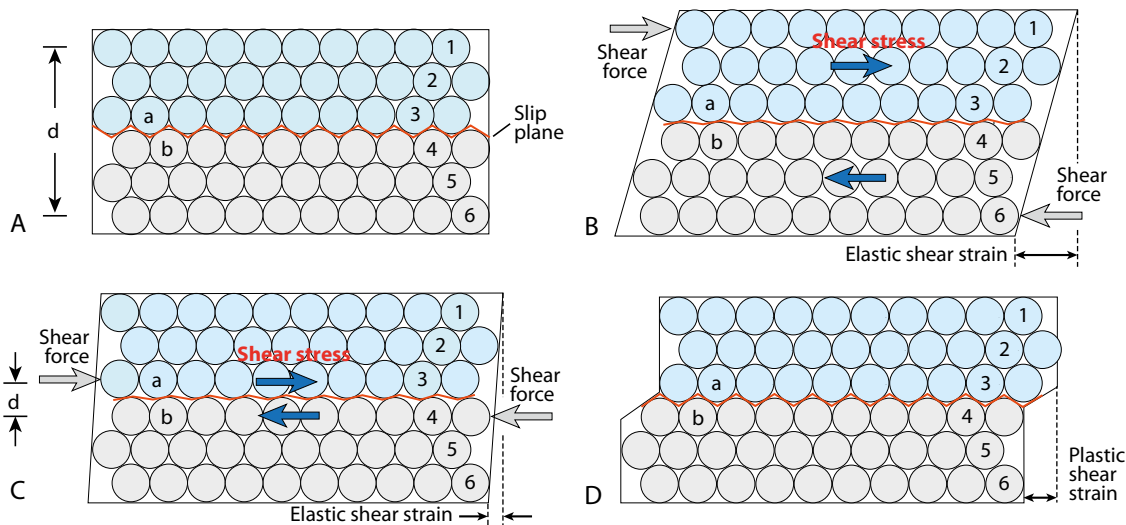
Strength

The stress and strain of a material under load was defined earlier. The challenging nature of the oral cavity, to which dental materials are subjected, was presented in Chapter 1 (*Challenges of Dental Materials in the Oral Cavity*). How can it be known if dental materials can survive in this harsh environment? Clinicians must use a material and decide on the dimensions of the restoration or prosthesis in such way that the material will safely withstand various occlusal-loading conditions. For specific dental materials, we are equally interested in the maximum stress that a structure can sustain before this material becomes plastically deformed and subsequently fractures. For this purpose, having information regarding the elastic properties and strength characteristics of materials under various stress conditions, which were discussed earlier, is imperative. *Strength* is the stress necessary to cause either a specified amount of plastic deformation (i.e., yield strength) or fracture (i.e., breaking strength) of the material. The term *elastic properties* refers to the stress-strain relationship during elastic deformation. Hooke's law of elasticity, also known as *Hooke's law*, states that the stretching of a solid body (e.g., metal, wood) is proportional to the force applied to this structure when the material behaves elastically. There is, however, a limit for each material, and this linear relationship is known as the **proportional limit**. These strength properties will be discussed in detail, along with their clinical significance, later in the chapter.

Information on the elastic properties and strength of materials can be obtained only through experimental investigations that use well-defined, well-configured, and standardized specimens, and subject these to comparatively simple stress conditions. Testing machines are designed to induce certain typical deformations of test specimens, such as tension, compression, shear, torsion, and bending (flexure). They also record the forces applied and the deformation the test specimens can sustain until fracture occurs. The maximum load recorded before the fracture of the specimen and the original dimension of the specimen are used to calculate tensile strength, compressive strength, shear strength, torsional strength, and flexural strength. For each dental material where strength values are needed as part of the specification, there are testing protocols established by TC 106–Dentistry of the International Organization for Standardization (ISO). Following these protocols is important for the standardization of testing methods.

Figure 4-4 shows a material represented by six rows of atoms under different states of shear stress. The zigzag line indicates the plane where the movement between rows of atoms would occur and is called the *slip plane*. The atoms on either side of the slip plane are shaded differently for contrast. Figure 4-4, A shows the relative locations of labeled atoms without stress. When a pair of forces from opposite directions acts on the top and bottom rows of the material, thereby subjecting the material to shear forces (Figure 4-4, B), the positions of the atoms shift in response to the shear stress generated within the material. Note the change in position between atoms a and b; atoms 1, 2, and 3; and atoms 4, 5, and 6. The overall change is the elastic shear strain, which will return to zero when the shear force is removed (Figure 4-4, A). If the shear force is increased sufficiently to move the atoms in row “a” farther to a new stable position, and then removed, a permanent slip (plastic deformation) along the slip plane occurs (Figure 4-4, D).

If the pair of forces is applied to the row of atoms directly above and below the slip plane (Figure 4-2, C), the relative position shift of atoms a and b will appear similar to the displacement seen in Figure 4-4, B, but the relative positions of atoms farther above the



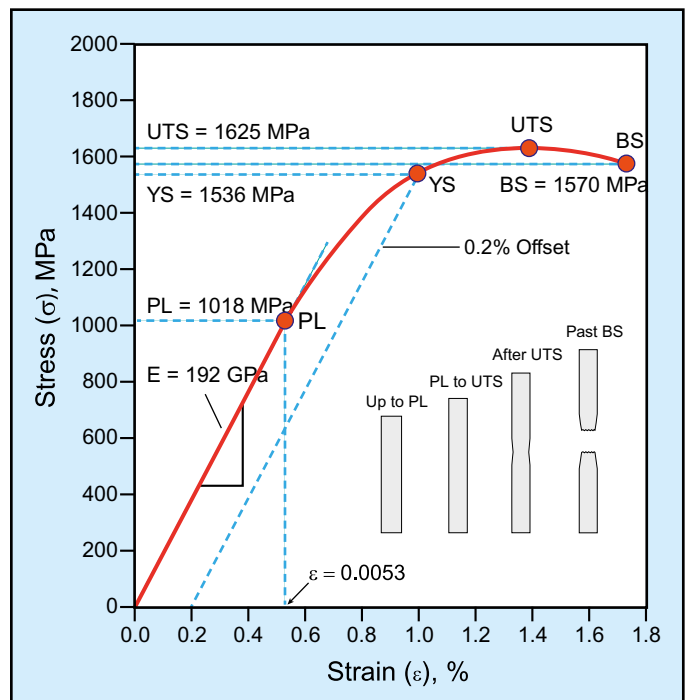
• **Figure 4-4** Atomic model illustrating deformation by shear force. **A**, No stress. **B**, Elastic deformation of the model under shear forces applied along the top and the bottom of the model. **C**, Elastic deformation by shear forces along the opposite side of the slip plane; note the difference in the quantity of the elastic strain by the movement of the atoms relative to that shown in (B). **D**, Plastic deformation as the atoms have moved to new positions and the forces are relieved.

slip plane, such as 1, 2, and 3, and atoms farther below the slip plane, such as 4, 5, and 6, will remain the same (Figure 4-4, C). As the shear force is increased and then removed when the row of atoms moves to the next stable position, the arrangement of atoms will register the same permanent deformation (Figure 4-4, D). Recall the discussion of moment of force. When the force is applied at a distance from the interface (Figure 4-4, B), the moment increases; therefore less force is needed to induce the same plastic deformation. This is the reason most shear tests for bonding systems do not truly measure shear bond strength.

Stress-Strain Properties

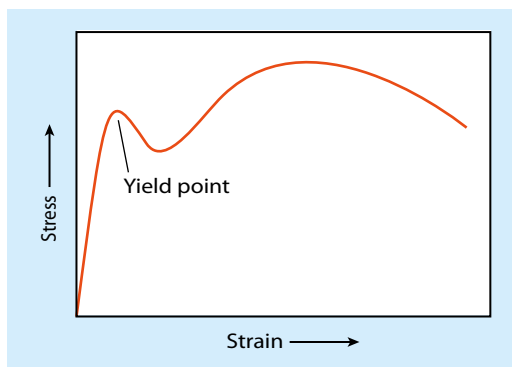
Figure 4-5 shows a stress-strain graph for a stainless-steel orthodontic wire that has been subjected to a tensile force. The solid orange line shows the stress (σ) obtained from forces divided by the cross-sectional area as the strain (ϵ) increases from stretching. The shape of the curve is typical for a tensile test. As the test begins, the stress-strain curve moves linearly toward the upper right, then starts to deviate from a straight line after passing the proportional limit (PL). The upward or y-axis movement is further reduced as the graph moves past the yield strength (YS). As the movement continues farther to the right, the line reaches a plateau at the ultimate tensile strength (UTS) and eventually breaks at a lower stress at the breaking strength (BS).

Imagine that we are in control of the tensile testing machine and observe the stress-strain plot recording in real time on the screen. Let us stop the experiment before the stress reaches PL and unload the wire; we will observe that the curve traces back to the zero stress and strain as the wire completes the elastic recovery to the original length. The linear segment of the curve is the graphical illustration of Hooke's law of elasticity. We can restart the test, and then stop immediately after the stress-strain curve has passed the proportional limit and unload. We still observe complete elastic recovery of the wire, which indicates that Hooke's law does not apply beyond the proportional limit, but the material deformation at that stress level remains elastic only. This process can be repeated with increasing stress levels and soon reach a point where



• **Figure 4-5** Stress-strain plot for a stainless-steel orthodontic wire that has been subjected to tension. The proportional limit (PL) is 1020 MPa. Although not shown, the elastic limit is slightly higher than that value. The yield strength (YS) at a 0.2% strain offset from the origin (O) is 1536 MPa, and the ultimate tensile strength (UTS) is 1625 MPa. The breaking strength (BS) is 1570 MPa. An elastic modulus (E) value of 192 GPa is calculated from the slope of the elastic region ($= PL/\epsilon$). Note the shape change of the wire as the tensile test progresses: the width of the wire contracts, necking after UTS and fracture.

the wire still exhibits elastic recovery but does not revert back to the original length, thereby exhibiting plastic deformation. Meanwhile, the rate of stress increase with respect to the strain reduces substantially. Normally, we describe that the stress has exceeded the **elastic limit** of the material, which is the stress level when



• **Figure 4-6** Yield point of a linear polymer. Note the downturn of the curve, indicating substantial necking after the material past the yield point.

plastic deformation occurs. Unfortunately, there is no notable feature on the curve that enables us to identify the stress level of the elastic limit. To find a convenient and practical substitute, we commonly draw a line parallel to the straight portion of the curve, starting at a value of 0.2%, along the strain axis and extend it until this line intersects with the curve. This stress value is designated the *0.2% offset yield strength* or *proof stress*. The significance of yield strength will be discussed later. From this point on, more plastic deformation of the wire develops after each stretch and unload. The stress then reaches a maximum value at the ultimate tensile strength, and the wire begins to show signs of necking, which is a reduction of the diameter in one area of the wire (specimen illustration in Figure 4-5). As stretching continues, the level of stress decreases until the wire fractures at the breaking strength, with all the plastic deformation that occurred after the ultimate tensile strength concentrating around the area of necking.

Proportional Limit, Elastic Limit, and Yield Strength (Proof Stress)

When a wire is stretched steadily in tension, the wire eventually fractures. However, in dentistry, we are also interested in the stress at which plastic deformation begins to develop, which is called the *yield point*. Softer metals and thermoplastic polymers show a pronounced yield point (Figure 4-6). This occurs at slightly higher stress levels than the elastic limit. At the yield point, the material shows a sudden increase of strain with no increase in stress. Materials specific for dental applications do not usually exhibit this behavior (Figure 4-5); thus a different approach is needed to determine the yield point.

For a material that satisfies Hooke's law, the elastic stress must be directly proportional to the elastic strain. Graphically, the initial region of the stress-strain plot must be a straight line, as shown in Figure 4-5. In fact, a small portion of the elastic deformation appears to be nonlinear before the onset of plastic deformation, which is demonstrated by the curve deviation from the straight line. The point of deviation is called the *proportional limit*, which represents the maximum stress above which stress is no longer proportional to strain.

When a small tensile stress is induced in a wire, the wire will return to the original length when the load is removed. If the load is increased progressively in small increments, and then released after each increase in stress, a stress value will be reached at which the wire does not return to the original length after the load is

removed. At this point, the wire has been stressed beyond the material's elastic limit, which is the greatest stress to which the material can be subjected to where the material will return to the original dimensions when the force is released. The value of the elastic limit, when available, is used as the yield point of the material. As discussed earlier, a stress-strain curve, such as that shown in Figure 4-5, does not show the stress of the elastic limit. However, for certain materials, experiments have shown that the stress values of the elastic limit are very close to their respective proportional limits. For those materials, the use of the values of the proportional limit as the yield point is customary.

CRITICAL QUESTION

Yield strength is a commonly reported property for metals and alloys but not for ceramics. Why is it not possible to measure the yield strength of ceramics or other purely brittle materials? Use a stress-strain plot to explain your answer.

For materials such as stainless steel, a good portion of the elastic deformation appears nonlinear, so the use of the proportional limit as the yield point is inappropriate. In addition, irregularities along the straight-line region of the stress-versus-strain plot may represent minor deviations from Hooke's law and cause some uncertainty in determining the appropriate point at which the selected line deviates from linearity (proportional limit). Thus a different property, **yield strength**, is used in cases where the proportional limit cannot be determined with sufficient accuracy.

Yield strength is a property that represents the stress value at which a small amount of plastic strain has occurred. A value of either 0.1% or 0.2% of the plastic strain is often selected and is referred to as the *percent offset*. As in Figure 4-5, the yield strength for 0.2% offset is illustrated. If yield-strength values for two materials tested under the same conditions are to be compared, identical offset values should be used. For brittle materials such as dental ceramics, the stress-strain plot is a straight line with no appreciable plastic region. Thus a determination of yield strength is not practical at either a 0.1% or 0.2% strain offset because there is no plastic strain.

Proportional limit, elastic limit, and yield strength (proof stress) are defined differently for the respective phenomena that occur during mechanical testing. However, they have been used interchangeably when referring to the yield point. Their values are usually very close but can be different in some cases. The elastic limit is the true yield point when this value is available. The proportional limit is used as the yield point when the proportional limit is well defined on the stress-strain curve and known to be close to the elastic limit. The yield strength is easy to obtain from a stress-strain curve with a preset amount of plastic deformation. Remember that the yield strength is defined with some plastic deformation in mind, but the proportional and elastic limits cover elastic deformation only. As shown in Figure 4-5, the yield strength (proof stress) is greater than the proportional limit. These values are important in the selection of dental materials because they represent the stress at which permanent deformation of the structure begins. If stresses generated during chewing exceed these values, the restoration or appliance may become distorted and no longer function as originally designed.

Imagine a patient biting on a bolus of food, as shown in Figure 4-3, exerting enough load to generate tensile stresses at the area noted as tension of the bridge alloy. As the patient gradually applies the load, the tensile stress in these areas will increase

proportionally to the magnitude of the load applied. If the stress generated is below the elastic limit and up to the proportional limit, the removal of the load will always result in an elastic recovery of the bridge from the slight bending that occurs. If the patient at any time exerts a load that creates stresses in the tension area that are equal to or exceed the elastic limit of the material used, the bridge will be permanently deformed, and then break. Accordingly, one must choose materials with adequately high elastic limits for the construction of a dental bridge. If the size of the connector is too small, greater tensile stress is generated. A properly designed restoration is also important.

Elastic Modulus (Young's Modulus or Modulus of Elasticity)

Hooke's law states that stress and strain change proportionally within the region of elastic deformation. Mathematically, there is a constant between the stress and the strain. We call this constant the **elastic modulus**, **modulus of elasticity**, or **Young's modulus**, designated by the letter *E*. The elastic modulus (*E*) of the orthodontic wire used in Figure 4-5 can be calculated as follows using the proportional limit (1018 MPa) and the elastic strain (0.0053) of this material:

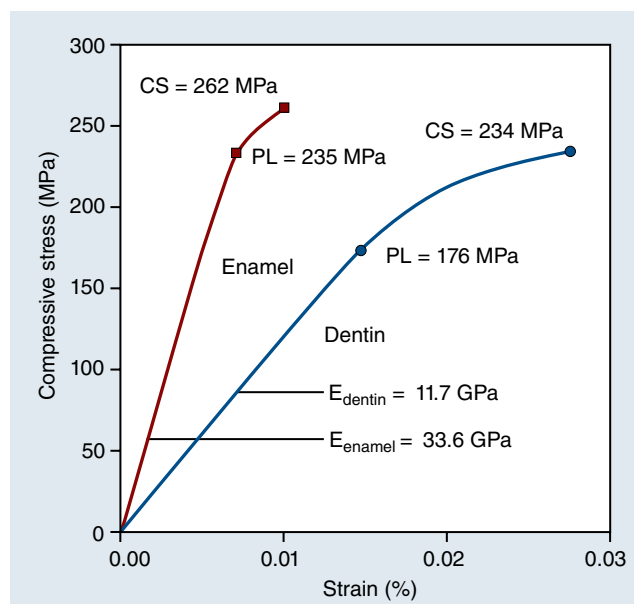
$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{\sigma}{\varepsilon} = \frac{1018 \text{ MPa}}{0.0053} = 192,075 \text{ MPa} = 192 \text{ GPa}.$$

(3)

Because the elastic modulus represents the ratio of the elastic stress to the elastic strain, we can reason that the lower the strain recorded for a given stress, the greater the value of the modulus. For example, if wire A is much more difficult to bend than wire B of the same shape and size, considerably higher stress must be induced before a desired elastic deformation can be produced. As such, wire A is considered to have a comparatively higher modulus of elasticity than wire B. Thus wire A, with a higher modulus of elasticity, stretches less than wire B under the same stress. Elastomeric impression materials have a greater stiffness (elastic modulus) than alginate-based impression materials. Thus a greater force is needed to remove an elastomeric impression tray from undercut areas in the mouth. The modulus of elasticity of most dental biomaterials is given in units of either MPa or GPa (gigapascals; 1 GPa = 1000 MPa).

In general usage, the term *elasticity* also implies "being easily stretched or expanded," which contradicts what we just learned: that a material with a high elastic modulus requires more force to deform. In fact, elasticity in solid mechanics describes the ability of a strained body to recover this body's original size and shape after deformation. This statement does not imply if straining the material is easy or difficult based on the stress applied. Therefore the elastic modulus is a parameter that quantifies the elastic behavior. We can also state that the elastic modulus describes the relationship between stress and strain within the elastic region. Some would state that the elastic modulus is the slope of the initial straight portion of the stress-strain curve. The steeper the line, the higher the elastic modulus and the stiffer the material. As such, the elastic modulus has been considered a measurement of the stiffness or rigidity of a material.

Recall Figure 2-2, *A*, in which bond force is defined as the attraction between two atoms, and Figure 4-4, *B*, which shows the distance between atoms under the influence of shear stress, such as the distance between atoms 2 and 3 and between atoms 4 and 5. The zero resultant force at equilibrium represents the material that



• **Figure 4-7** Stress-strain plot for enamel and dentin that have been subjected to compression. The ultimate compressive strength (CS), proportional limit (PL), and elastic modulus (*E*) values are shown. (Data from Stanford JW, et al: Compressive properties of hard tooth tissue. *J Am Dent Assoc* 60:746–756, 1960.)

is not under stress. The change in distance between atoms increases with respect to the external force applied and should follow the curve of resultant force in Figure 2-2. The slope of resultant force drawn from the equilibrium position will have the same meaning as the slope of the stress-strain curve. Because the force needed to change the distance between atoms depends on the bond strength between atoms, the value of the elastic modulus reflects the atomic bond strength of the material, which remains constant and independent of mechanical treatment, such as the stress applied, and the plastic deformation incurred during the test.

Figure 4-7 shows a stress-strain graph for enamel and dentin that have been subjected to compressive stress. These curves were constructed from the typical values of elastic moduli, proportional limit, and ultimate compressive strength reported in the scientific literature. Variations in the values of the proportional limit, elastic modulus, and ultimate compressive strength have been reported for enamel and dentin relative to the area of the tooth from which the test specimens were obtained. Note that the proportional limit, ultimate compressive strength, and elastic modulus of enamel are greater than the corresponding values for dentin (Figure 4-7). The elastic modulus of enamel is about three times that of dentin in this study. Dentin can sustain more plastic deformation than enamel under compressive loading before dentin fractures. Thus enamel is a stiffer and more brittle material than dentin, and unsupported enamel is more susceptible to fracture. Conversely, dentin is more flexible and tougher. Although there is no quantifiable measurement for the brittleness of a material, we often describe materials as being more brittle or less brittle. We refer to more brittle materials as having less elastic deformation before fracture and less brittle materials as having more elastic deformation before fracture.

Recall Figure 3-2, which shows a Newtonian fluid exhibiting a linear relationship between the shear stress and strain rate of the fluid, and the slope of the curve is defined as the viscosity of the liquid. Figure 4-5 shows that there is a linear relationship between the tensile stress and strain of a solid, and the slope defines the

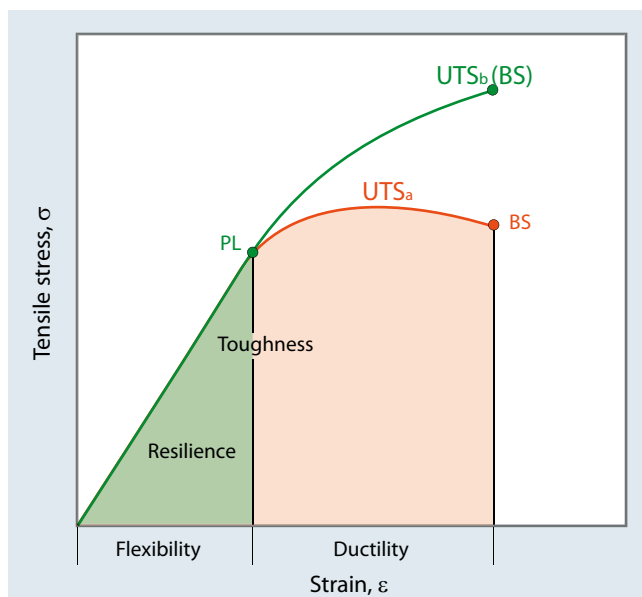
elastic modulus of a solid. Both terms are derived from the stress and strain relationship; they represent two different properties. The elastic modulus is the quantity that dictates how much the material will deform elastically for a given stress and remain at that state forever unless the stress is removed, at which time, the material returns to its initial shape. The viscosity is the analogous quantity that shows how fast the material will flow and the change of strain in proportion to the duration that the stress is applied.

CRITICAL QUESTION

How can the ultimate tensile stress (ultimate strength) sometimes be less than the maximum tensile stress?

Ultimate Strength and True Strength

Ultimate strength for tensile, compressive, and shear tests is calculated by dividing the maximum force recorded before fracture by the original cross-sectional area of the material. The specimen configuration shown in Figure 4-5 demonstrates that the cross section of the wire decreases as the wire lengthens under tensile stress. Because of the reduction in area, the force required to increase deformation decreases. Thus the stress calculated past the ultimate tensile strength decreases, leading to a breaking strength that is lower than the ultimate tensile strength. Figure 4-8 shows a stress-strain plot of a metal rod that has been subjected to a tensile test. The stress is calculated using the original cross-sectional area (orange line) and the actual cross-sectional area (green line). The stress value, calculated as the force divided by the actual cross-sectional area at each measured strain value, is known as **true stress**. The green line shows that the ultimate tensile strength and



• **Figure 4-8** Conventional tensile stress-strain curve (orange line) in the plastic deformation region calculated using the initial cross-sectional area of a rod. The green line (above the orange line) represents the calculated stress values based on the actual reduced area of the rod as deformation increases. Note that the ultimate tensile strength (UTS) value of the green line is the same as the breaking strength (BS). The resilience can be calculated by measuring the area within the elastic region. Mathematically, the area is half of the proportional limit (PL) multiplied by the elastic strain (equation [4]). The toughness is the total area within the elastic and plastic regions.

breaking strength are the same. The original dimension is always used to calculate the various strength values reported—and for good reason. The failure of a restoration or device means that either yielding or rupture has occurred, whichever came first. Damage has occurred at a lower load, and therefore a higher and more precise value of true ultimate strength is not meaningful.

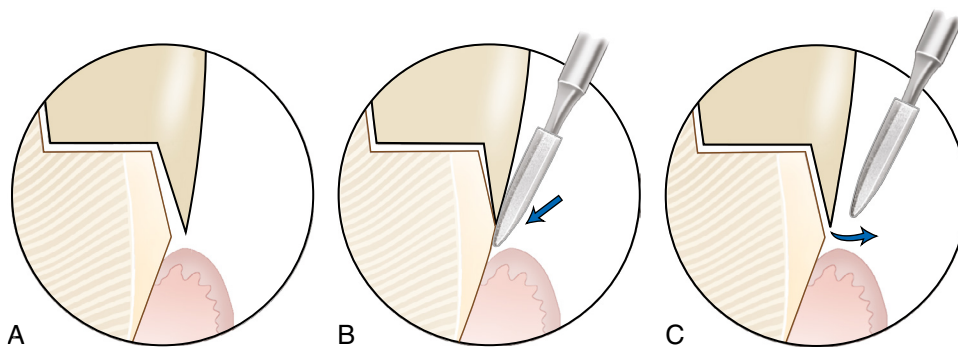
Figure 4-8 demonstrates that after a metal rod has been stressed beyond this material's yield point, the stress needs to increase to continue exerting plastic deformation until fracture of the specimen occurs. One may think that the material has a fixed yield point; once the stress applied has overcome that barrier, the same level of stress should be enough to induce further plastic deformation until the specimen fractures. The true stress of Figure 4-8 shows that the material that has been plastically deformed is resisting further yielding because more stress is required. Indeed, the material becomes stronger with respect to resisting further plastic deformation, as it is plastically deformed until it fractures, and this phenomenon is known as **strain hardening**, **work hardening**, or **cold working**. We will learn the mechanism of material strengthening by plastic deformation in Chapter 9, **Dislocation Movement in Polycrystalline Alloys**.

Flexibility and Ductility

From the stress-strain curve, we know that for each stress value, there is a corresponding strain value. Having a material with sufficient strength to resist plastic deformation or fracture is not the only consideration for selection. However, there are instances where elastic and plastic deformation are critical. For example, in an orthodontic appliance, a spring is often extended a considerable distance under the influence of a small stress. In such a case, the structure is said to be flexible and possesses the property of flexibility. *Flexibility* is defined as the elastic strain shown on a stress-strain curve (Figure 4-8) or the reversible flexural strain of a bending test. Ductility represents the amount of permanent deformation a material can sustain under a tensile load up to the point of fracture, which is the deformation from the proportional limit to the breaking strength in Figure 4-8. **Malleability** is the amount of permanent deformation a material can sustain without rupture under compression, such as hammering or rolling a metal rod into a thin sheet. Gold is the most ductile and malleable pure metal, followed by silver. Of the metals of interest in dentistry, platinum ranks third in ductility, and copper ranks third in malleability.

Ductility can be determined in one of three ways: (1) the percent elongation after fracture as seen in Figure 4-8, (2) the reduction in area of tensile test specimens, and (3) the maximum number of bends performed in a cold-bend test before the wire fractures. The first method involves taking the information directly from a stress-strain curve. The second method involves necking at the fractured end of a ductile metal wire after rupture under a tensile load. The percent decrease in cross-sectional area of the fractured end in comparison with the original area of the wire or rod is referred to as the *relative reduction in area*. The third method is known as the *cold-bend test*. We can bend several orthodontic wires back and forth individually until they all break. The wire that takes the greatest number of bends to break is the most ductile wire.

Burnishing of a cast metal margin to reduce the width of a gap between the crown margin and the tooth surface is a good example of flexibility and ductility at work. Figure 4-9 shows a burnishing procedure of an open metal margin (Figure 4-9, A), where a smooth, dull instrument is used as a burnishing tool to press the metal margin against the tooth (Figure 4-9, B) and close the



• **Figure 4-9** Schematic illustration of a procedure to close an open margin of a metal crown by burnishing with a dull instrument shaped like a rotary instrument. **A**, The margin of the crown is open. **B**, The instrument pulls down the margin and press toward the tooth to “close” the margin. **C**, Note that after the instrument is removed, the elastic strain of the crown rebounds; a slight marginal discrepancy remains. To reduce the size of discrepancy, one needs to pull down the metal farther toward the gingival to compensate for the elastic recovery.

marginal gap. This movement is possible as a result of the elastic plus plastic strain of the metal. After the instrument is removed, the margin springs back an amount equal to the total elastic strain (Figure 4-9, C). Because at least 25 μm of space must be provided for the cement between the tooth and the crown, total burnishing on the tooth or die is usually adequate because the amount of elastic strain recovery is relatively small. Pushing the margin further while pressing against the tooth to compensate for the anticipated elastic recovery may be required. Naturally, the metal should have relatively high ductility to prevent fracture of the margin during burnishing and moderate yield strength to facilitate the procedure.

Resilience and Toughness

Work is the product of the force times the amount of deformation (distance) through which the force acts. When work is performed on a body, energy is imparted to this body. Consequently, when a dental restoration is deformed, the restoration absorbs energy. If the induced stress is less than the proportional limit (i.e., the oral structure is not permanently deformed), only elastic energy is stored in the structure until the applied force is removed. **Resilience** (U_r) is the ability of a material to absorb energy when it is deformed elastically (Figure 4-8). The modulus of resilience is the amount of strain energy that can be absorbed per unit volume without permanent distortion and can be determined by the area of the elastic region:

$$U_r = \frac{1}{2} \sigma \epsilon = \frac{1}{2} \cdot \frac{\sigma^2}{E} \quad (4)$$

When the induced stress goes beyond the elastic limit of the material, additional work is needed to cause plastic deformation. The ability of a material to absorb energy and plastically deform without fracture is called **toughness**. The modulus of toughness is the amount of strain energy per unit volume that a material can absorb just before it fractures and can be calculated as the area under the stress-strain curve up to the fracture point.

Toughness increases with an increase in strength and ductility. The greater the strength and the higher the ductility (total plastic strain) are, the greater the toughness is. Thus we can conclude that a tough material is generally strong, although a strong

material is not necessarily tough. The term *brittleness* is generally considered to be the opposite of toughness. It is important to note that in popular terms, *resilience* is associated with springiness, which implies bouncing back from a deformation. In the present context, *resilience* precisely means the amount of strain energy absorbed within a unit volume of a structure being stressed to its proportional limit.

Poisson's Ratio

Because of the conservation of mass, an object, such as a cylinder, becomes longer and thinner when a tensile force is applied to it. Conversely, a compressive force acts to make such an object shorter and wider. An axial tensile stress, σ_z , along the z -axis (long axis) of a mutually perpendicular x, y, z -coordinate system produces an elastic tensile strain (ϵ_z) and an accompanying elastic contraction in the x - and y -directions (ϵ_x and ϵ_y , respectively). The ratio of ϵ_x/ϵ_z or ϵ_y/ϵ_z is an engineering property of the material called *Poisson's ratio* (ν), calculated as follows:

$$\nu = -\frac{\epsilon_x}{\epsilon_z} = -\frac{\epsilon_y}{\epsilon_z} \quad (5)$$

Poisson's ratio can be similarly determined in an experiment involving an axial compressive stress. For an ideal isotropic material of constant volume, the ratio is 0.5. Most engineering materials have values between 0.25 and 0.30.

Other Strength Test Methods

There exists a large number of standardized tests to determine the various mechanical properties of materials. Three types of tests relevant to dental materials are discussed.

Diametral Tensile Strength

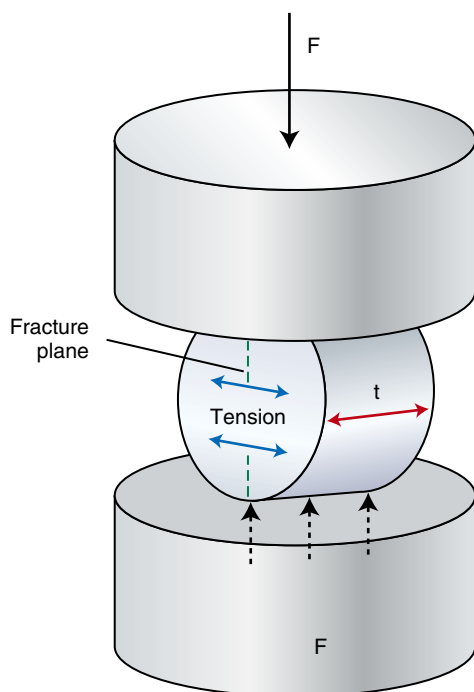
Tensile strength can be determined by subjecting a rod, wire, or dumbbell-shaped specimen to tensile loading. A lack of plastic deformation for adaptation to the gripping device of a conventional tensile test apparatus and alignment makes tensile tests for brittle materials difficult. However, when a short cylinder (disk)

is laid on the side with a load applied from the top along the diameter of the cylinder, the load generates tensile stress perpendicular to the vertical plane passing through the center of the disk (Figure 4-10), forcing the cylinder to expand laterally. This test is referred to as the *diametral compression test*, and the strength value obtained is the diametral tensile strength. In this method, the compressive load is applied by a flat plate against the side of a short cylindrical specimen (disk). Fracture should occur along this vertical plane (the dashed vertical line on the disk). The diametral tensile strength value is calculated by the following formula:

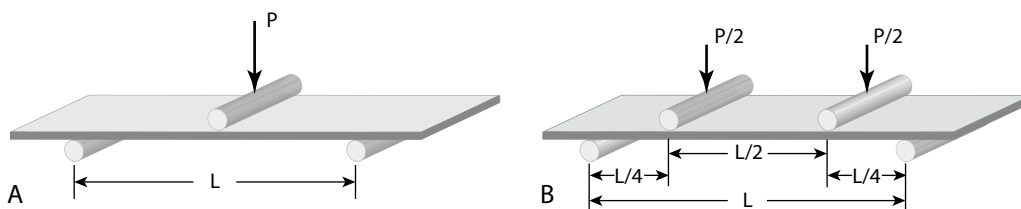
$$\text{Diametral tensile strength} = \frac{2F}{\pi Dt}, \quad (6)$$

where F is the applied load, D is the diameter of the disk, and t is the thickness of the disk.

This test is simple to conduct and provides excellent reproducibility. However, the use of this test on materials that exhibit appreciable plastic deformation before fracture results in erroneously high tensile-strength values. In addition, fracture of the specimen into several pieces rather than the ideal fragmentation into two segments suggests an unreliable test result.



• **Figure 4-10** Diametral compression test. Although a compressive force is applied along the side of the disk, a tensile fracture is produced. The tensile strength is calculated from the fracture load, F , the disk diameter, D , and the disk thickness, t .



• **Figure 4-11** Uniaxial flexure test designs. A, Three-point test. B, Four-point test.

Flexural Strength

Flexural strength measures the response of a material to bending and does not measure the fundamental material properties, which are tensile, compression, and shear strengths. During bending, all three fundamental stresses are present. The flexural test is a strength test of a bar supported at each end (Figure 4-11) or a thin disk supported along a lower support circle under a static load (Figure 4-12). The tensile stress usually develops along the lower surface, which is the supported side of the test specimen, and causes fracture. For the bar specimen, the failure stress value is referred to as the *uniaxial flexural strength*, *flexural strength*, *transverse strength*, or *modulus of rupture*. For the disk specimen, the failure stress value is referred to as the *biaxial flexural strength*.

Uniaxial Flexural Strength

When the load is applied, the flat bar specimen bends with tensile, compressive, and shear stresses generated simultaneously. The resulting strain is represented by a decrease in the length of the top surface (compressive strain) of the specimen and an increase in the length of the lower surface (tensile strain). Consequently, the principal stresses on the upper surface are compressive, whereas those on the lower surface are tensile. Obviously, the stresses change direction within the specimen between the top and bottom surfaces, with both stress and strain being zero at the transition. This neutral surface does not change in dimension and is known as the *neutral axis*. Shear stress is also produced near the supported ends of the specimen but does not play a significant role in the fracture process.

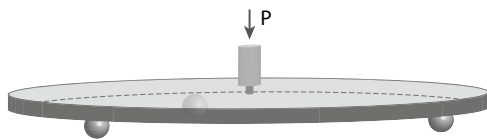
There are two different mode-of-flexure tests: three-point (Figure 4-11, A) and four-point (Figure 4-11, B). For rectangular cross-section bars, the following equations may be used to calculate the flexural strength:

$$\text{Three-point flexural } \sigma = \frac{3FL}{2wt^2}, \quad (7)$$

$$\text{Four-point flexural } \sigma = \frac{3FL}{4wt^2}, \quad (8)$$

where σ = flexural strength (MPa) at the midpoint of the span, P = the load (N) at fracture, L = the distance between two support rollers (mm), w = the width of specimen (mm), and t = the thickness or height of specimen (mm).

One of the limitations of the three-point flexural test is that if the bar specimen does not fracture at the midpoint directly under the applied force (F), the moment of force at the point of fracture should be used to calculate the fracture stress at the actual point of fracture. The four-point flexural test shown in Figure 4-11, B



• **Figure 4-12** Schematic illustration of the piston-on-three-ball test for the biaxial flexure test.

is preferred over the three-point test because the analyses of force balance indicate that there is no shear stress present, and the moment of force is constant within the central loading span where fracture is expected.

Flexural tests are preferred to the diametral compressive test when brittle materials are used in the construction of dental prostheses, such as cantilevered bridges, multiple-unit FDPs (or bridges), and complete dentures because the stress distributions in flexural tests more closely simulate those that occur in these prostheses.

Biaxial Flexural Strength

The edge of rectangular specimens often chips or fractures during preparation and can become an area of **stress concentration** influencing the strength values. The biaxial flexure test is based on the piston-on-three-ball design that directs the strain toward the center of the disk, away from the edge of the specimen (Figure 4-12). This test is preferred by some scientists to avoid the problem of edge effects. For the typical biaxial flexural tests, disk-shaped specimens 12 mm in diameter and 1.2 mm in thickness are used. The load is applied by means of a piston with a slightly curved contact surface, and the disk is supported by steel balls, which have a diameter of approximately 3.2 mm. These are arranged at an angle of 120° relative to each other on a circle of approximately 10 to 12 mm in diameter. The biaxial flexural strength is calculated from a complex equation that is beyond the scope of this book.

Impact Strength

The term *impact* describes the reaction of a stationary object to a collision with a moving object. A Charpy-type impact tester is usually used to measure impact strength. A pendulum is released that swings down to fracture a bar specimen with a V-notch in the center and supported at both ends. The energy lost by the pendulum during the fracture of the specimen can be determined by a comparison between the length the pendulum swings after impact with the pendulum's free swing when no impact occurs. The energy lost divided by the area of the fracture surface is the impact strength, with a unit of kJ/m². Unlike the case in most mechanical tests, the dimensions, shape, and design of the specimen to be tested should be identical for uniform results. This property may be defined as the energy required to fracture a material under an impact force. An Izod-type impact tester is like that of a Charpy, except the V-notch specimen is clamped vertically at one end, and the blow is delivered at a certain distance above the clamped end instead of at the center of the specimen.

During impact, the external forces and resulting stresses change rapidly; therefore a stress-strain curve cannot be used to predict the impact strength precisely, but it is a good indicator. For example, a material with a low elastic modulus and a high tensile strength is more resistant to impact forces, whereas a high elastic modulus and a low tensile strength suggest low-impact resistance.

CRITICAL QUESTIONS

How can two identical forces produce two different stresses in an all-ceramic crown? Is it possible for a stiff material with a high modulus of elasticity to fail with no plastic deformation and at a lower strength than a more flexible material? Explain your answers.

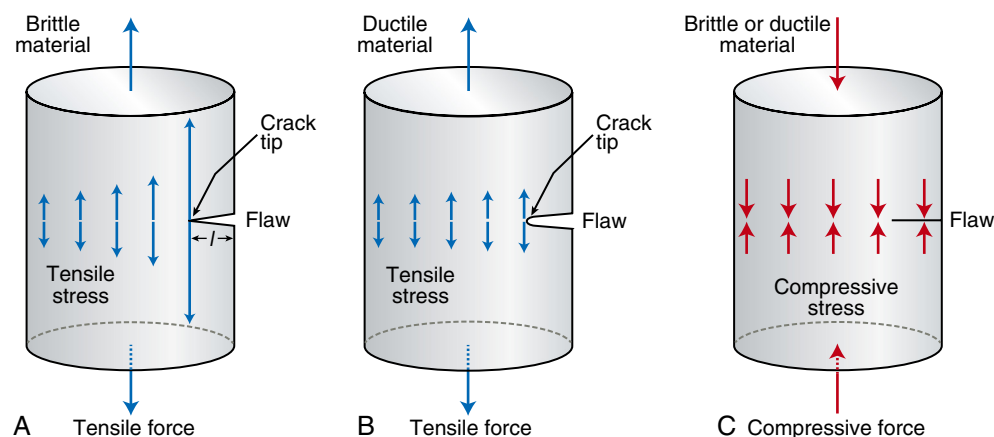
Fracture of Restorations

In one of his books, Leonardo da Vinci described an experiment where tensile strengths were measured for various lengths of iron wires. His finding was that longer wires were weaker than shorter wires. This result is inconsistent with the classical theory of what is now known. Unexpected fractures of dental prostheses and restorations occur occasionally even when high-quality materials have been used. From the point of view of fracture mechanics, both observations are related to the presence of small microstructural flaws and defects on the surface or within the internal structure that facilitate the generation of locally high stresses in areas near holes, grooves, notches, sharp corners, cracks, and other changes in the dimension of the structure even though the average stress within the structure is low. This increase in the peak-stress section is called the *stress concentration* or *stress riser*. During da Vinci's time, the technology of making iron wire was likely to produce inherent surface flaws that increased in number with longer wires. This in turn increased the probability of fracture of longer wires with a lower load.

Stress Concentration

Figure 4-13 shows an illustration of the theoretical tensile-stress distribution in brittle and ductile materials in the presence of a crack. The localized stress (σ_{LO}) at the tip of the crack is proportional to the square root of the ratio of the crack length (L) to the radius of the crack tip (ρ); the relationship is shown as $\sigma_{LO} \propto \sqrt{L/\rho}$. The crack tip in a brittle material is sharp (small radius) and does not deform plastically to relieve stress. Therefore the crack is prone to propagate as the localized stress increases to a critical level. Note the increased level of tensile stress at the tip of the flaw (Figure 4-13, A). However, the stresses at areas far away from these flaws are much lower. Although the tensile stress has increased at the flaw tip in brittle and ductile materials, stress has increased by a smaller amount in the ductile material (Figure 4-13, B), in which plastic deformation has occurred with subsequent widening of the flaw tip (increasing radius of the tip), thereby reducing the magnitude of localized tensile stress. The flaw does not play a significant role when the material is subjected to an external compressive force (Figure 4-13, C) because the compressive stress that develops in the material tends to distribute uniformly and close the crack.

Surface defects, such as porosity, grinding roughness, and machining damage, are common with brittle materials (e.g., ceramics, amalgams, and composites). These defects can be eliminated or reduced in depth by polishing. There are also interior flaws, such as voids or inclusions. Unfortunately, little can be done for interior flaws other than to ensure the highest quality of the structure during the fabrication stage. The design of any prosthesis involves marked changes in contour, such as the point of attachment of a clasp arm to a partial denture framework or a sharp internal angle at the pulpal-axial line angle of a tooth preparation for an amalgam or composite restoration. The transition areas often become sites of stress concentration. Any



• **Figure 4-13** Effect of surface flaw on the stress distribution of materials under tension and compression. **A**, Surface flaw on brittle material substantially increases the tensile stress at the tip of the flaw as a result of stress concentration. **B**, Plastic deformation at the tip of the surface flaw on the surface of ductile material reduces the intensity of stress concentration at the tip of the flaw. **C**, Surface flaws have no influence on the compressive strength as the tip of the flaw is pressed closed by compression.

change in contour should vary gradually rather than abruptly. Therefore notches should be avoided. The internal line angles of tooth preparations should be rounded to minimize the risk of cusp fracture.

Recall the discussion on the challenges of restorations in the oral cavity in [Chapter 1](#), thermal expansion in [Chapter 3](#), and elastic modulus earlier in this chapter. When a direct restoration is bonded to the tooth or a prosthesis is cemented to tooth structure, there is a difference in the elastic moduli and thermal expansion coefficients across the bonded interphase. As the interphase is being occluded or subjected to temperature change from food intake, the dimensions of all materials, including the tooth, change accordingly but are different in quantity. The differences in the quantity of changes can result in additional stresses in the interphase and initiate fracture of the weaker structure. It is not likely that all restorative materials used have elastic moduli and thermal expansion coefficients that closely match that of the tooth. Therefore the weaker, more brittle material should have the lower elastic modulus so that more stress is transferred to the material with the higher elastic modulus. The weaker, more brittle material should have a slightly lower expansion or contraction coefficient so that a protective compressive stress is sustained in the structure of this material next to the interface ([Chapter 10, Maximize Development of Residual Compressive Stresses](#)).

Unusually high stresses may occur when a load is applied over a small area of contact, also known as *point contact* or *Hertzian load*. This phenomenon typically arises on a microscopic scale when a force is transmitted through two bodies in contact. A clinical example is that of a cusp tip of an opposing crown or tooth that encounters another restoration. The cusp tip should be well rounded so that the occlusal contact areas on the brittle material are large and wide, leading to reduced stress. In addition, the internal line angle of the tooth preparation should have as large of a radius of curvature as possible to reduce Hertzian stress in the intaglio of the restoration.

In the following segment, we discuss some parameters that have been devised to characterize the role of flaws in the propagation of cracks within the materials.

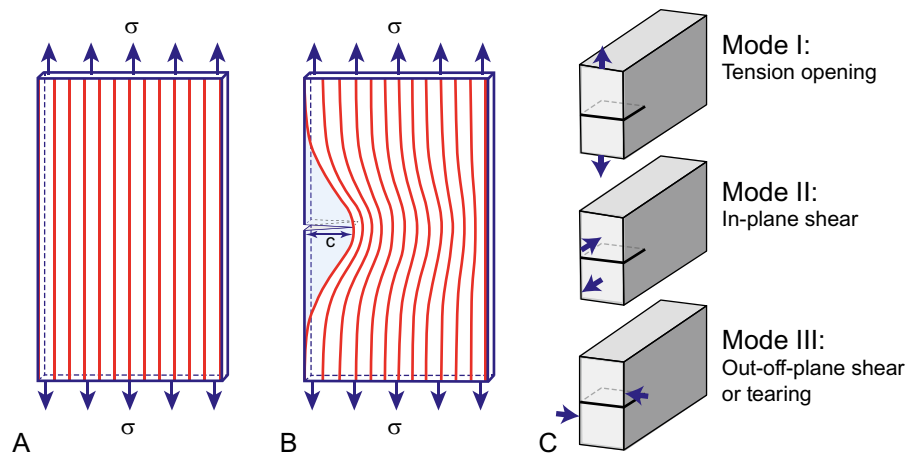
CRITICAL QUESTIONS

Fracture toughness is a more precise measure of the fracture resistance of a brittle material than the tensile strength. Why is the tensile strength of brittle materials—such as dental amalgam, composite, ceramic, and inorganic cements—so variable? Which one of a series of reported tensile strength values should be used in considering the selection of a new product made of one of these materials?

Fracture Toughness

For brittle materials, such as dental ceramics, strength is of limited value in the design of ceramic prostheses. Small defects (porosity and microcracks) are randomly distributed in location and size throughout a ceramic, causing large strength variations in otherwise-identical ceramic specimens. Alan Griffith in 1920 proposed that the failure of brittle materials occurs at the largest flaw of the material. He invoked the thermodynamics energy conservation law to formulate a fracture theory. Recall from the discussion of resilience ([Figure 4-8](#)) that when an object is stressed elastically, there is strain energy stored within the object ([Figure 4-14, A](#)). The presence of flaws in a stressed body reduces the volume of the solid under stress and thus the strain energy that would have been stored in the shaded area around the notch in [Figure 4-14, B](#). Meanwhile, the total surface energy of the object increases, reflecting the increase in the surface area of the object resulting from the presence of the notch.

The Griffith theory postulates that when the strain-energy reduction from the presence of the notch is less than the total surface energy of the notch surface, nothing happens at the tip of the notch. However, this balance of energy changes as the external stress increases. The quantity of the strain-energy reduction that would have been stored in the shaded area increases, whereas the surface energy of the notch surface remains the same because there is no change to the size of the notch. When the projected strain-energy reduction in the shaded area exceeds the surface energy of the notch surface, a crack will propagate from the tip of the notch and continue until the object fractures. Griffith further developed a relationship between the stress at failure and the flaw size (the notch) based on balancing the reduction of strain energy that



• **Figure 4-14** Energy-balance approach of Griffith criterion of fracture and modes of fracture. **A**, An illustration of uniform stress distribution within an object under tensile force. The overall energy of the stressed object is the total of the surface energy of the object and the strain energy stored in the object ($= \frac{1}{2} \cdot \frac{\sigma^2}{E} \cdot V_0$, where V_0 is the volume of the object). **B**, The effect of a notch with the depth of “c” on the stress distribution of the same specimen under the same tensile force. The shaded area represents the volume (V) of the object that does not store strain energy. The overall energy of the stressed object decreases by the amount of strain energy that would have been stored in the shaded volume ($= \frac{1}{2} \cdot \frac{\sigma^2}{E} \cdot V$). However, the object gains surface energy from the surface of the notch ($= 2\gamma_c \cdot c \cdot t$). γ_c is the surface energy, c is the depth of the notch, and t is the thickness of the object. **C**, Three modes of stressing condition to enable propagation of preexisting cracks. Arrows show the direction of forces.

occurs during fracture with the increase in surface energy resulting from the creation of new free surfaces when a crack grows. The analysis gave the following result:

$$\sigma_f = \sqrt{\frac{2\gamma_c E}{\pi c}}, \quad (9)$$

where σ_f is the failure stress, c is the flaw size, γ_c is the surface energy, and E is the elastic modulus. Because γ_c and E are intrinsic material properties, the value of $\sqrt{2\gamma_c E}$ should be a constant for the material of the same composition being tested, and the equation can be rearranged as $\sqrt{2\gamma_c E} = \sigma_f \sqrt{\pi c}$. The relationship embodies that scatter in the measurement of fracture stress (σ_f) arises from the variation in the size of flaw (c). The term $\sigma_f \sqrt{\pi c}$ is known as **stress intensity factor** (K_{Ic}) or **fracture toughness**, and $K_{Ic} = \sigma_f \sqrt{\pi c}$ is the expression that describes the severity of the stress state at the crack tip.

The scenario just discussed leads to the conclusion that during fracture, new surfaces are created to release the elastic strain energy stored during stressing. Under static-loading conditions, the work required to extend the crack by the unit length is equal to the dissipated elastic-strain energy. Therefore for brittle materials, the term $2\gamma_c$ is also called the *critical strain-energy release rate* (G_c , for Griffith), and $G_c = 2\gamma_c = K_{Ic}^2 / E$; the factor 2 is needed because a pair of equal-size free surfaces has evolved for every crack.

There are three ways of applying a force to enable a crack to propagate experimentally, as shown in **Figure 4-14, C**: mode I is commonly called the *opening-mode loading*, mode II corresponds to shearing of the crack face that occurs with in-plane shear stresses, and mode III is a tearing action driven by out-of-plane shear stresses. The fracture toughness of a material determined under tension using a standard configuration with a known flaw

size is given by the symbol K_{Ic} (the subscript *I* refers to mode I fracture) in units of $\text{MPa} \cdot \text{m}^{1/2}$. The Griffith relationship is often expressed as follows for a mode I fracture:

$$K_{Ic} = \sigma_f Y \sqrt{c_{\text{crit}}}, \quad (10)$$

where c_{crit} is the critical flaw size that initiates propagation when the stress reaches σ_f . Note that Y is a geometrical factor that comprises $\sqrt{\pi}$ shown in **equation (9)**. The use of K_{Ic} in the literature means that the experimental specimens used are not of standard configuration with a known flaw size.

Fracture toughness (critical-stress intensity) is a mechanical property that describes the resistance of brittle materials to the catastrophic propagation of flaws under an applied stress. Thus the fracture resistance of a porcelain veneer with a K_{Ic} value of $0.75 \text{ MPa} \cdot \text{m}^{1/2}$ is much lower than that of the tougher supporting core ceramics used for ceramic-ceramic prostheses, such as alumina, with a K_{Ic} value of $3.4 \text{ MPa} \cdot \text{m}^{1/2}$, and yttrium-stabilized zirconia, with a K_{Ic} value of $7.9 \text{ MPa} \cdot \text{m}^{1/2}$. Keep in mind that the toughness of the material discussed earlier is about the energy needed to fracture the material and comprises both elastic deformation and plastic deformation if fracture occurs.

CRITICAL QUESTION

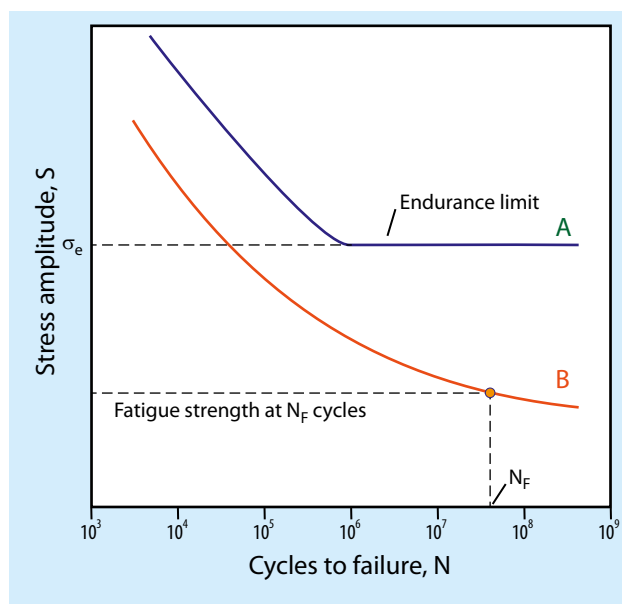
Is a stiff material (high elastic modulus) stronger than a more flexible material? Explain your answer by sketching a stress-strain plot.

Fatigue Strength

Strength values obtained from measurement of the failure loads described in earlier tests are based on one loading cycle to failure. Clinically, these strength tests can be misleading because these

restorations are subjected to repeated or cyclic loading and need to be designed to withstand these recurring forces. Normal mastication induces several thousands of stress cycles per day within a dental restoration without showing visible signs that would lead to fracture. After a period of service, failure can occur without warning during normal mastication. Most prosthesis and restoration fractures develop progressively over many stress cycles after the initiation of a crack from a critical flaw that subsequently propagates until a sudden, unexpected fracture occurs. Stresses well below the ultimate tensile strength of the material can produce premature fracture of a dental prosthesis because microscopic flaws grow slowly over many cycles of stress. This phenomenon is called *fatigue failure*. The stress required to produce failures in a specified number of cycles is called *fatigue strength* or *endurance strength*. For glasses and certain glass-containing ceramics, the induced tensile stress and the presence of an aqueous environment further reduce the number of cycles to cause fatigue failure.

Fatigue behavior can be represented by an S–N diagram (Figure 4-15), which is determined by subjecting a series of specimens to a constant cyclic-stress amplitude (S), which is the amount that the stress deviates from the mean cyclic stress, and the number of loading cycles (N) until the specimen fails. Millions of cycles might be required to cause failure at lower loading levels, so the abscissa is plotted logarithmically. In some materials, the S–N curve flattens out eventually so that below a certain endurance limit (σ_e), failure does not occur no matter how long the loads are cycled (curve A of Figure 4-15). Thus, when the applied stress from mastication is below the endurance limit of the material, the restoration is said to be free from fatigue failure. For other materials that do not exhibit well-defined endurance limits, such as curve B of Figure 4-15, we can specify a desirable life cycle N_F , which is set at 5×10^7 cycles in Figure 4-15, and identify the corresponding stress amplitude. The value of this stress amplitude is the fatigue strength. For brittle materials with rough surfaces, the endurance limit is lower than would be expected if the surfaces were highly polished.



• **Figure 4-15** Typical S–N curve of fatigue test. Curve A shows the material exhibiting an endurance limit. Curve B exhibits no well-defined endurance limit; however, the effective endurance limit (fatigue strength) can be acquired by specifying the desired loading cycles (N_F) before failure.

Some ceramic materials exhibit a phenomenon referred to as *static fatigue* or *delayed failure*. These materials will support high static loads for a long period of time, and then fail abruptly under the same load. This failure is believed to result from a stress-dependent chemical reaction between water vapor and the ceramic surface, which alters the shape and/or depth of surface flaws. The flaw size lengthens over time, the magnitude of tensile stress that can be sustained by the ceramic is reduced, and eventually, the ceramic fails under the same load.

Weibull Modulus

The strength of an object or a material most often refers to the maximum stress required to cause fracture or plastic deformation. After repeating the experiment, we find that the breaking-strength values of all specimens are not the same. We group the measured values and calculate the mean and standard deviation to show the variation of the strength values. That information shows that about 50% of the tested specimens have failed below this strength. If we wanted to know the stress level below which 95% of specimens of identical shape, size, and processing conditions would survive a given fracture test, we would find that the mean and standard deviation cannot provide an exact value of the breaking strength wanted. The reason is that calculation of the standard deviation is based on the normal distribution of the strength values. We learn that crack propagation initiated at the inherent surface flaws are the causes of failure at the stress levels recorded. If the flaws are distributed uniformly throughout the entire pool of specimens, then the breaking strength must be about the same for all specimens. The fact that there is always a range of values indicates that flaws are clustered inconsistently among test specimens. In addition, strength values from mechanical tests are typically asymmetrical.

Let us assume that in a group of specimens, there is a definite probability of fracture (P_f) occurring on each specimen when this is subjected to a specified level of stress (σ), and the value of P_f monotonously increases with the stress. For a group of specimens tested, if each specimen had been subjected to a stress lower than the lowest strength value of the group, the probability of any specimen to fracture is $P_f = 0$, and if a stress greater than the highest value of the group had been used, then $P_f = 1$. Therefore each strength value of the group is associated with the P_f of the specimen. The strength of a material can possibly be presented as a distribution of values rather than as one specific mean value with standard deviation. How do we formulate such a distribution?

Waloddi Weibull in 1937 devised a distribution function, now known as the *Weibull distribution*, that fits the values of σ and P_f discussed earlier and calculates the parameters. The following equation is the two-parameter (σ_0 and m) version of the Weibull distribution:

$$P_f = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right], \quad (11)$$

where P_f = fracture probability defined by the relation $P_f = i/(N + 1)$,

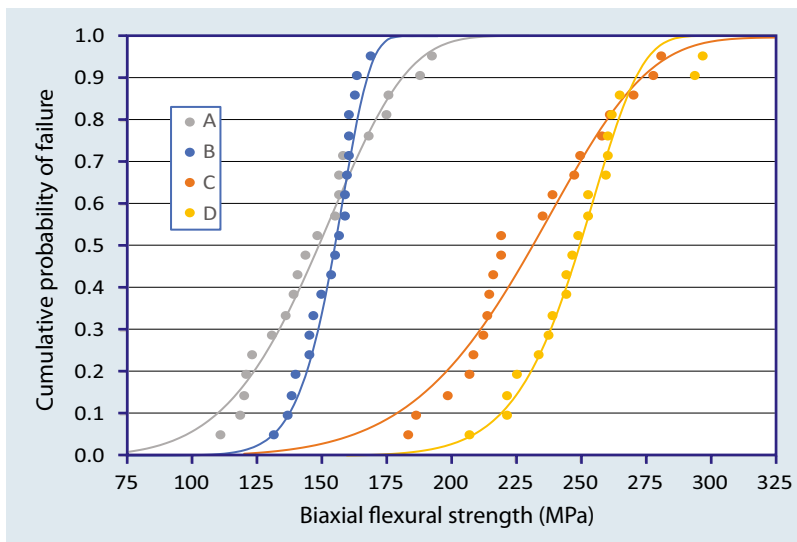
i = rank of the strength value σ_i ,

N = total number of specimens in the sample,

m = shape parameter or Weibull modulus,

σ = fracture strength as measured, and

σ_0 = scale parameter or characteristic strength.



Weibull Analyses

Material	Characteristic Parameter	Weibull Modulus	Strength of 1% Failure Rate
A	158.1	7.6	86.3
B	158.2	19.0	124.2
C	242.5	9.7	150.9
D	258.8	13.8	185.4

Descriptive Statistics

Material	Mean Strength	Standard Deviation
A	149.0	23.8
B	153.6	10.4
C	231.0	29.3
D	249.0	22.4

• **Figure 4-16** Illustration of Weibull distribution. **A**, Weibull plot of four materials showing biaxial flexure-strength values with respect to the calculated probability of failure and the best-fit curve by equation (8). **B**, Result of Weibull analyses and descriptive statistics of the same data set. (Experimental data courtesy Dr. Hae-Hyoung Lee, reported in Choi B-J, Yoon S, IM Y-W, et al: Uniaxial/biaxial flexure strengths and elastic properties of resin-composite block materials for CAD/CAM, *Dent Mater* 35:389–401, 2019.)

To use this equation, we first sort the strength data of a test group with N specimens in the order of lowest to the highest and assign each strength value a P_f value by dividing the rank (i) of the strength value by $(N + 1)$. The strength values with corresponding P_f values were fitted in the distribution function to determine the values of parameters σ_0 and m . With the knowledge of these two values, the stress of the projected failure rate can be calculated. Figure 4-16 presents experimental data by Weibull distribution and normal distribution.

These calculations are based on data obtained on a representative population (ideally 30 or more) of specimens tested in a manner similar to that which the materials will experience during clinical service. A low Weibull modulus value reflects a high variation in measured strength values with a high standard deviation (materials A and C in Figure 4-16), and the size range of the material's physical flaws, whether inherent to the material or resulting from the manufacturing process, are clustered inconsistently. There is an increase in the probability that flaws will interact with each other to weaken a brittle material. The use of these products for prostheses will result in a greater variation in fracture force and decreased reliability. Higher values of the Weibull modulus correspond to a higher level of homogeneity of the material, such as lower values of standard deviation, and greater reliability as a structural material.

Weibull plots of cumulative probability of failure as a function of fracture stress (Figure 4-16) can be used as a factor in the design of dental restorations made from brittle biomedical materials. If a dental practice specifies that less than 1 restoration in 100 could fracture during use, the Weibull distribution data can be used to estimate the stress that would cause this 1% level of failure. With a knowledge of this 99% survival stress, the design of restorations can be optimized by changing dimensions or restricting use conditions such that no region within the restoration sustains stresses above the failure stress. The power of Weibull distribution will be discussed further in Chapter 18, *The Weibull Size Effect*.

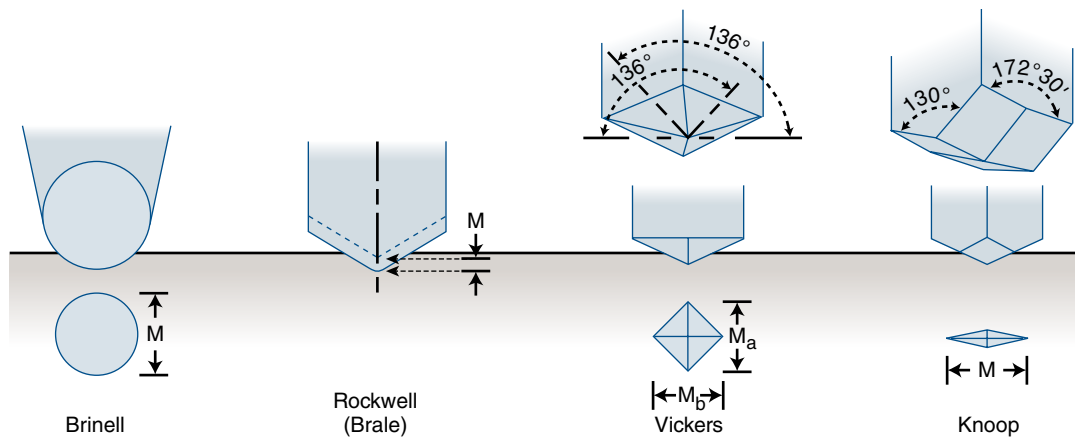
Properties of Surface Interactions

The loading situation shown in Figure 4-3 focuses on the stress distributed through the restoration in response to external forces. One may ask what is happening at the point of contact where the force is applied. In fact, the material at the point of contact responds differently from the rest of the material. If the applied force is delivered by the cusp tip of the opposing tooth followed by a horizontal movement, sliding occurs at the point of contact. The localized response to an applied load is characterized by **hardness**; however, the sliding results in *friction* at the interface and the restoration. Friction can cause *wear* of both objects involved. These properties are discussed in the following sections.

Hardness

In mineralogy, the relative hardness of a substance is based on the ability to resist surface scratching. In metallurgy and most other disciplines, the generally accepted concept of hardness is the “resistance to penetration” by a well-defined configuration of indenter made of a specific material. On the stress-strain curve, the material first resists elastic deformation, yields after the elastic limit, and then undergoes plastic deformation. When the indenter is removed, all elastic deformation recovers, but a permanent marking is left. An indentation produced on the surface of a material is the result of the interaction of numerous properties, such as elastic modulus, compressive strength, proportional limit, and ductility. The tests most frequently used in determining the hardness of dental materials are known by the names *Brinell*, *Rockwell*, *Vickers*, *Knoop*, and *Shore*.

In the Brinell hardness test, a hardened steel ball is pressed under a specified load into the polished surface of a material, as diagrammed in Figure 4-17. The load is divided by the area of the projected surface of the indentation, and the quotient is referred to as the *Brinell hardness number*, usually abbreviated as BHN, or HBW, when tungsten carbide ball is used. Thus for a given load,



• **Figure 4-17** Shapes of hardness indenter (*upper row*) and the indentation depressions left in material surfaces (*lower row*). The measured dimension M that is shown for each test is used to calculate hardness. The following tests are shown: In the Brinell test, a steel ball is used, and the diameter of the indentation is measured after removal of the indenter. In the Rockwell test, a conical indenter is impressed into the surface under a minor load (*dashed line*) and a major load (*solid line*), and M is the difference between the two penetration depths. In the Vickers or 136° diamond pyramid test, a pyramidal point is used, and the diagonal length of the indentation is measured. In the Knoop test, a rhombohedral pyramid diamond tip is used, and the long axis of the indentation is measured.

the smaller the indentation, the larger the number and the harder the material.

The Rockwell hardness test is like the Brinell test in that a steel ball or a conical diamond point is used (Figure 4-17). Instead of measuring the area of indentation, the depth of penetration is measured directly by a dial gauge on the instrument. Different sizes of indenters are available for testing a variety of materials. The Rockwell hardness number (abbreviated as RHN) is designated according to the indenter and load employed. The convenience of the Rockwell test, with direct reading of the depth of the indentation, has led to the wide usage of this test in industry. However, neither the Brinell test nor the Rockwell test is suitable for brittle materials.

The Vickers hardness test uses a square-based pyramid (Figure 4-17). Calculation of the Vickers hardness number (usually abbreviated as HV or VHN) is the same as that for the BHN in that the load is divided by the projected area of indentation. The lengths of the diagonals of the indentation are measured and averaged. The test is suitable for determining the hardness of brittle materials; therefore this test has also been used for measuring the hardness of other cast dental alloys and tooth structure.

The Knoop hardness test employs a diamond-tipped tool that is cut in a geometrical configuration (Figure 4-17). The indentation is rhombic in outline, and the length of the largest diagonal is measured. The load is divided by the projected area to give the Knoop hardness number (usually abbreviated as HK or KHN). When the indentation is made and the indenter is subsequently removed, the shape of the Knoop indenter causes elastic recovery of the projected indentation to occur primarily along the shorter diagonal. The stresses are distributed in such a manner that only the dimensions of the minor axis are subject to change by relaxation. Thus the hardness is virtually independent of the ductility of the tested material.

The Knoop and Vickers tests are classified as microhardness tests in comparison with the Brinell and Rockwell macrohardness tests. They give average hardness values over much larger areas. Both the Knoop and Vickers tests employ loads of less than 9.8 N. The resulting indentations are small and limited to depths of less than $19\ \mu\text{m}$.

The Shore hardness test is for elastomers that do not yield to permanent indentation for measurement. Instead, this test

measures the depth of an indentation in the material created by a given force using a scale of 0 (soft) to 100 (hard). The principle of the test is also based on resistance to indentation. The hardness number is based on the depth of penetration of the indenter point into the material. This hardness test is used mainly for the hardness of extraoral maxillofacial materials.

Friction and Wear (Tribology)

When we write on a blackboard with a piece of chalk, we feel there is a resistance between the chalk and the blackboard. Meanwhile, we do not feel any stickiness between the chalk and the blackboard as we lift the chalk between writing. This action leaves a trail of chalk dust that adheres to the blackboard. If some cooking oil is spread on the board surface, we will feel less resistance during writing and observe no trail of the dust on the board. The resistance felt during writing is called *friction*. The friction effects are those that arise from the tangential forces transmitted across the interface of contact when solid surfaces are pressed together by our hands. No stickiness indicates there is no appreciable amount of adhesion between the chalk and the board. The chalk dust is the result of the process of wear, and the trail is the result of adhesion. The wear phenomena consist of the removal of material from the surfaces of one of the contacting bodies as a result of interaction with the other contacting body. Adhesion is the ability of contacting bodies to withstand tensile force after being pressed together. The layer of oil on the board surface keeps the chalk from contacting the blackboard, which effectively eliminates wear of the chalk. In engineering terms, this process is called *lubrication*. In dental material manipulation, this behavior has been used to keep materials from sticking together. For example, a separating medium is used to keep denture resin from adhering to the gypsum mold in denture processing (Chapter 11, *Preparation of the Mold*).

Tribology is the term referring to the study and application of the principles of friction, wear, and lubrication. The following segment focuses on friction and wear as they occur during clinical service.

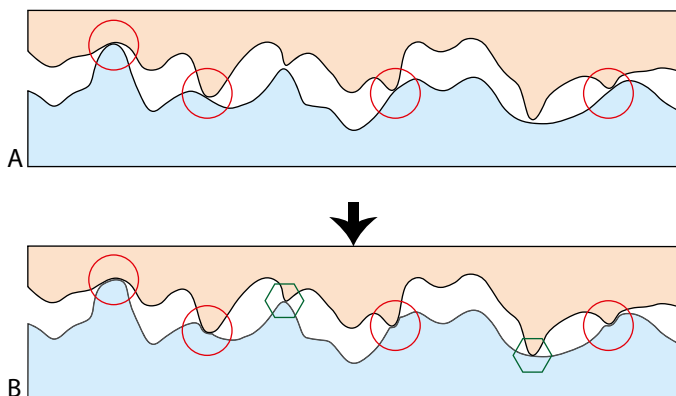
Friction

Friction is the force that opposes the relative motion that exists when a solid object is moved tangentially with respect to the surface of another that this object touches or when an attempt is made to produce such motion. Although friction is an obstacle to motion, the presence of friction makes the completion of certain tasks possible. We fight against friction as we walk or drive to a destination; however, we need the friction to stop the motion when we reach the destination. In the dental office, operators holding various instruments in their hands, such as a tool for condensing amalgam or scaling teeth, cannot carry out their work if the friction between the operator's hand and the instrument is too low. When this occurs, we call that condition "slippery." Take the RPD as an example, the friction between the retentive clasp and the abutment tooth plays an important role in keeping the RPD stable.

Mechanism of Friction

Macroscopically, a surface may look shiny as light is reflected well from the surface. The same surface in submicron scale could look like a mountain terrain filled with peaks called *asperities* (Figure 4-18). Consider two solid materials stacked upon each other; there are points of contact called *asperity junctions* (Figure 4-18, A), and the sum of the areas of all the junctions constitute the *real* area of contact, A_r . The interfacial area between the two surfaces is known as the *apparent surface area* (A_a) as observed by our eyes.

Because the real area of contact is only a small fraction of the apparent surface area, the stress at each junction could be one or several magnitudes higher than that calculated using the apparent surface area. One or both materials may be plastically deformed. The harder asperity will dent the softer one, as shown in Figure 4-18, B, when additional load is applied. Recall the discussion in Chapter 2, *Types of Bonding*, that attractions between atoms and molecules occur at a very short range, on the order of magnitude of only a few Angstroms. If both surfaces are free of contaminants, the stress at the asperity/asperity interface can be high enough to cause bonding at the atomic or molecular level, forming asperity junctions. To begin sliding between



• **Figure 4-18** Microscopical aspect of the interface between two objects. **A**, The weight of the top object is supported by the bottom object at the points of contact. **B**, Additional pressure causing more deformation of the bottom object and additional areas of contact. This illustration indicates that the top object is harder than the bottom one. If one is to slide the top object horizontally to the right, it needs to overcome the obstacles of the bottom object at the areas of contact. The force needed to break through is the friction, and fracture of asperities of either object at the contact could occur. The residue of fracture asperities is the wear debris.

opposing surfaces, these junctions need to be broken. As the sliding continues, asperities of opposing surfaces collide, which can result in fracture of the weaker asperities or harder asperities plowing through the softer surface. The combined effort to make the object move is reflected in the frictional force.

The friction is expressed in quantitative terms as a force. The initial force needed to start sliding is called *static friction*, and the force needed to continue sliding is called *kinetic friction*. The force required to begin sliding is greater than the force needed to keep the object sliding.

Laws of Sliding Friction

The following are the laws of friction expressing the magnitude of the friction force as a function of macroscopically observable variables: the applied load, the size of the region of contact, and the sliding velocity:

1. The friction force F is proportional to the normal force P : $F = \mu P$. This relationship enables us to calculate the coefficients of static friction, μ_s , and kinetic friction, μ_k .
2. The friction force is independent of the apparent area of contact, A_a . Thus large and small objects have the same coefficients of friction. Keep in mind that the interaction that occurs at the real areas of contact is what contributes to friction. Additional load increases the real area of contact but not the apparent area of contact (Figure 4-18, B).
3. The kinetic friction force is independent of the sliding velocity. This implies that the force needed to maintain sliding is the same at any specified velocity.

Friction plays important roles in various dental appliances and instruments. For example, we can consider static friction as a mechanism for preventing a restoration from falling off its intended location.

Wear

Wear may be defined as the removal of material from solid surfaces as a result of mechanical action. The wear process is generally thought of as destructive because it often leads to failure of prostheses or appliances. In fact, there are a considerable number of practical uses for the wear process. Here are some examples where controlled wear is needed to accomplish the work: In the making of a composite restoration, there is a need to shape the restoration and finish to a pleasing appearance. Finishing involves a sequence of abrasive processes. Among these are the use of burs, abrasive paper, and finally, loose abrasive grains to achieve a very smooth surface. In cutting operations as part of cavity preparation, having a sharp edge for the cutting tool is essential. If during the operation, the edge becomes blunted, cutting no longer occurs; the process must be stopped, and the edge must be re-formed.

Types of Wear

Research has established that there are four main forms of wear: (1) adhesive, (2) abrasive, (3) corrosive, and (4) surface-fatigue wear. Each wear process obeys its own laws; however, on many occasions, one of the modes of wear acts in such a way as to affect the others.

Adhesive wear results from the strong bonding that occurs whenever atoms or molecules come into intimate contact under pressure. The asperity junctions are broken near the interface within one of the materials during sliding. In consequence, a transferred fragment will be formed. That fragment might be broken off when this fragment collides with another asperity from the opposing material. The repeated process of asperity-junction

formation, fracture near the junction, and detachment of transferred fragments yields debris of adhesive wear.

Abrasive wear arises when a hard, rough surface slides against a softer surface, digs into this surface, and plows a series of grooves. The material originally in the grooves is normally removed in the form of loose fragments, or else the material forms a pair of mounds along each groove. A harder surface is less likely to wear than a softer surface because the harder surface resists denting, but the softer surface does not. This is known as *two-body abrasive wear*. Abrasive wear can also arise in a somewhat different situation, when hard, abrasive particles are introduced between sliding surfaces and abrade material from each surface. The mechanism of this form of abrasive wear seems to be that an abrasive grain adheres temporarily to one of the sliding surfaces or is embedded in the material and plows out a groove in the other. This is known as *three-body abrasive wear*.

Corrosive wear occurs in situations where the environment surrounding a sliding surface interacts chemically with the surface. If the products of reaction are worn off the surface, corrosive wear has occurred. The first stage of corrosive wear is corrosive attack of the surface, which is identical with ordinary corrosion. Some corrosion processes can result in a protective layer that slows down the corrosion process, such as with aluminum, titanium, and alloys with sufficient chromium. The second step of the corrosive wear process consists of wearing away the reaction product film, as a result of sliding, and exposing a fresh surface for corrosive attack.

Surface-fatigue wear is closely related to the general phenomenon of fatigue of materials in that there is a characteristic interrelation between the stresses in the contacting materials and the number of cycles required to produce fracture. As stressing and unloading of the material of occluding continue, a subsurface crack propagates. For a long time, the material appears to be quite unaffected by this stress cycling, but suddenly, perhaps after a few hundred thousand hours of loading, a particle spalls off the surface, and thereafter, deterioration of the surface and flaking of fragments become rapid.

There are a few marginal processes that are often classified as forms of wear that include actions of fretting, erosion, cavitation, and impact. Each type describes a different way in which the load and sliding action are introduced. Briefly, *fretting wear* arises when contacting surfaces undergo oscillatory tangential displacement of small amplitude. *Erosion wear* is a process in which a particle carried in a fluid medium hits a solid surface and removes material from this surface. *Cavitation-erosion wear* occurs as a result of the cavitation of a liquid. The liquid is put through a cycle of compression, then tension, and then compression again, and so on. *Impact wear* is a short sliding motion, such as grit-blasting, where two solid bodies interact for an exceptionally short time interval.

Factors Influencing Abrasive Wear

The amount of abrasive wear in volume loss (V) is found to be proportional to the size of the actual contact area. This actual contact area is proportional to the pressure applied (P) and inversely proportional to the hardness of the surface (H). In addition, the wear increases as the distance of travel by one surface increases. In dentistry, the distance is often in the form of the chewing cycle (N). Mathematically, the relationship is expressed as $V \propto (N \cdot P / H)$. This equation does not necessarily hold true in all cases but clearly points out the influence of three major factors on wear. In reality, many other factors may be involved in the wear process,

such as surface roughness, temperature, and environment (e.g., moisture). Roughness increases the actual contact area and the wear. Polishing to attain a smooth surface is highly advisable to reduce wear. The thermal properties of the surface become important when sliding takes place at high speeds, such as grinding and polishing. The oral environment provides natural lubrication that reduces wear. Soft foods reduce wear because they serve to cushion and lubricate during mastication. The resulting wear debris may be washed away by saliva or may be trapped between the two opposing surfaces, creating so-called three-body abrasive wear. This phenomenon occurs when the diet is impregnated with fine, solid particles and during brushing of the teeth with an abrasive.

Improvement of Wear Resistance

According to the mathematical relationship described in the last section, hardness is the only material-related factor that can be altered to influence wear behavior. For polymers, there are two ways to improve wear resistance: one is to increase the molecular weight during polymerization, and the other is to incorporate fine particles of high strength and hardness. For example, the wear resistance of resin composite is substantially improved by the addition of fine ceramic particles or glass beads and increasing the degree of cure of the resin during polymerization ([Chapter 5, Fillers](#)). To reduce the impact of wear, the selection of the opposing material is of paramount importance. For example, porcelain teeth should not be allowed to oppose natural dentition or resin composite restorations.

CRITICAL QUESTION

Why do prostheses sometimes fail under a very small force even though the strength of the prosthetic material is relatively great?

Strength of Tooth Structure

The relatively wide variation in mechanical properties of human tooth structure is attributed to the technical problems associated with preparing and testing such small specimens, which in some instances are less than 1 mm in length. The results reported in one study are shown in [Table 4-1](#). This study investigated the effect of enamel-rod orientation by propagating cracks in the occlusal surface and in axial sections in directions parallel and perpendicular to the occlusal surface. The cracks in the axial enamel section were longer in the direction perpendicular to the occlusal surface rather than parallel to the surface. The cracks that propagated toward the dentinoenamel junction (DEJ) were arrested and did not penetrate the DEJ into dentin. The fracture toughness of dentin varied by a factor of 3 as a function of enamel-rod orientation. The elastic modulus of enamel also varied between the occlusal surface and the axial section. The results of this study demonstrate that the mechanical properties of tooth structure are a function of microstructural orientation. Indentation energy is a recently introduced property that is used to predict the machinability and wear behavior of ceramics. Research data suggest that during indentation or cutting, brittle enamel may be removed by microfracture, whereas dentin may be removed by forming ductile chips.

Although the data in [Table 4-1](#) indicate a variation in the properties of enamel and dentin from one type of tooth to another, the difference is more likely the result of variations within individual teeth than between teeth. The properties of enamel vary somewhat

TABLE 4-1 Properties of Tooth Structure (Human Third Molars)

Microhardness Indentation Method	Occlusal Enamel	Axial Enamel	Dentin
Hardness (GPa)	3.23	3.03	0.58
Toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	0.77	0.52 (⊥) 1.30 ()	—
Hardness (GPa)	3.62	3.37	0.57
Toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	94	80	20
Indentation energy (μJ)	2.6	2.7	7.5

⊥, Enamel axial section perpendicular to occlusal surface; ||, enamel axial section parallel to occlusal surface.

From Xu HHK, Smith DT, Jahanmir S, Romberg E, Kelly JR, Thompson VP, Rekow ED: Indentation damage and mechanical properties of human enamel and dentin. *J Dent Res* 77:472–480, 1998.

with the position on the tooth; that is, occlusal enamel is stronger than enamel on other surfaces of the tooth. Also, the properties of enamel vary according to the microscopic structure. For example, enamel is stronger under longitudinal compression than when subjected to lateral compression. On the other hand, the properties of dentin appear to be independent of structure, regardless of the direction of compressive stress.

The tensile properties of tooth structure have also been measured. Dentin is considerably stronger in tension (50 MPa) than enamel (10 MPa). Although the compressive strengths of enamel and dentin are comparable, the proportional limit and modulus of elasticity of enamel are greater than the corresponding values for dentin. The higher modulus of elasticity of enamel results in less resilience compared with dentin.

Typically, the energy of a biting or chewing event is absorbed by the food bolus during mastication and by the teeth, periodontal ligament, and bone. Also, the design of the tooth enables the tooth to absorb significant static and dynamic (impact) energies. As can be seen in [Figure 4-7](#), the modulus of resilience of dentin is greater than that of enamel and is better able to absorb impact energy. Enamel is a brittle substance with a comparatively high modulus of elasticity, a low proportional limit in tension, and a low modulus of resilience.

CRITICAL QUESTION

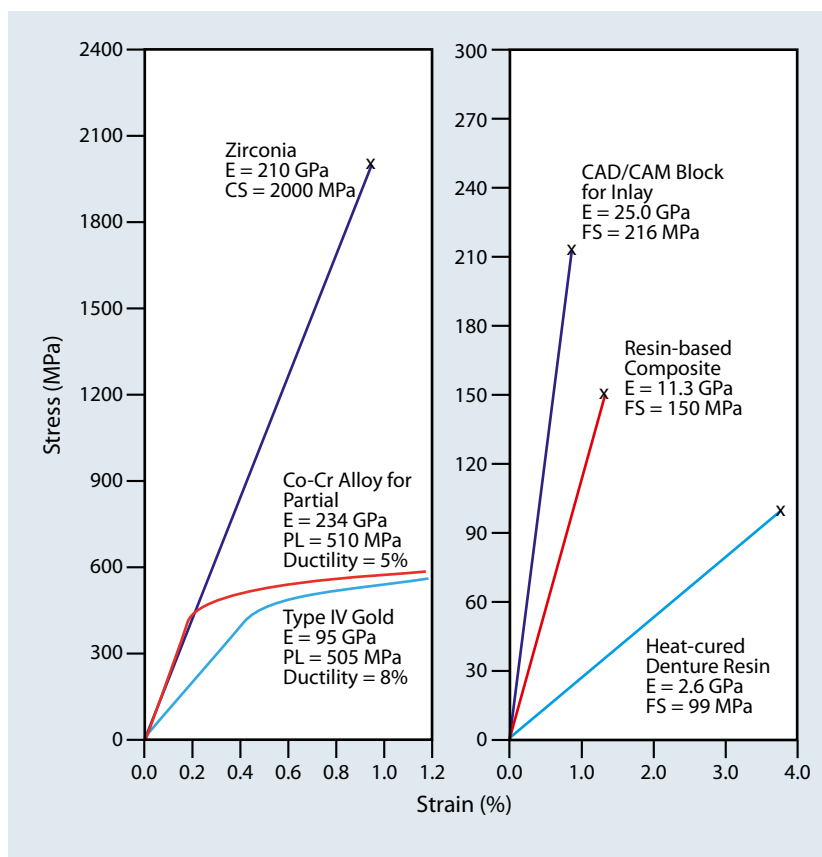
What is the difference in appearance between a stress-strain graph for a material that has high strength, high stiffness, and high ductility and one for a material that is weak, flexible, and more brittle?

Selection of Dental Materials

Deciding on the best treatment option is a multifactor task that involves the condition of the tooth to be restored, the patient's condition and desire for an esthetic appearance, and the clinician's preference and prior experience. The next step is selecting the type of restorative material made of any of the four general classes of materials discussed in [Chapter 2](#). The design of the prosthesis or the cavity preparation often depends on the physical ([Chapter 3](#)) and mechanical characteristics of the type of material selected. The goal is to distribute the stresses uniformly within the prosthesis or the supporting tooth or tissue substrates and avoid stress concentration for the longevity of the restorations. You will learn more about the principles of design in respective operative and prosthodontic classes. Here, we examine how to select suitable materials based on their mechanical characteristics to facilitate treatment options.

When the responses of materials to external forces are observed from a stress point of view, they are described in terms of proportional limit, elastic limit, yield strength (proof stress), ultimate strength, and breaking strength. If the concern is about deformation, they are described as brittle or ductile, and their flexibility, ductility, and malleability are measured. If the ability of the devices to dissipate impact energy during service is required, their moduli of resilience and toughness must be calculated. All categories of these descriptions can include fracture. When a restoration fractures, should this be attributed to a lack of strength, shortness in ductility, or not enough toughness? The answer depends on the function of the prosthesis and how the material fractured. The fracture of a mesial-occlusal-distal (MOD) composite restoration resulting in the loss of a proximal box could have been caused by poor preparation design that led to a stress concentration that eventually weakened the strength of the restoration. During the adjustment of the clasp of an RPD, we can easily break the clasp after numerous episodes of adjustment, but pulling the clasp apart by tension would be impossible. Continuous bending of the clasp consumed this material's ductility and resulted in the fracture of the clasp as the ductility was exhausted. A denture that is accidentally dropped on a hard floor and breaks indicates that the denture cannot absorb all the energy from impact, and that this excess energy is dissipated by the denture fracturing. Depending on the potential mode of fracture, the selection criteria could change.

Fracture is not the only concern for material selection. From the previous discussion of the three-unit FDP ([Figure 4-3, A](#)), we realize that elastic deformation occurs in the form of flexing as load is applied on the pontic. Flexing can cause the two abutment teeth to be pulled laterally toward the pontic. This action can cause loosening of the abutment teeth or cement debonding over time. If the span of the FDP increases as additional pontic units are added, the degree of flexing multiplies. Using a material of greater elastic modulus will limit the elastic deformation relative to the force applied. For RPDs, the metal framework needs to be rigid to maintain the denture's fit for uniform distribution of the stresses on the supporting soft tissues. Rigidity of the framework can be achieved with proper design and the selection of materials that have greater elastic modulus. The retentive clasp discussed earlier may require mechanical properties that are different from that of the framework, especially the ability to be adjusted without fracture. The framework and the retentive clasps can be made separately and joined together later through soldering. Even though high elastic moduli are often associated with high-strength materials, it is important to emphasize that the elastic modulus addresses only the correlation of the stress and strain during the elastic deformation. We will discuss in



• **Figure 4-19** Stress-strain curves of six commercial products representing four general classes of materials. The mechanical properties shown are elastic modulus (E), proportional limit (PL), flexure strength (FS), compressive strength (CS), and ductility.

Chapter 13, Elasticity and Viscoelasticity, that an elastic modulus much lower than those of metals and ceramics is essential for making impressions.

The stress-strain curves of six commercial products for four classes of materials are shown in **Figure 4-19** in two plots. Most of the restorative materials available are brittle, except for metals. We should emphasize that *brittle* simply refers to the inability of a material to deform plastically before fracture. Brittleness is not associated with the strength of a material, even though most high-strength materials used in dentistry are brittle. The brittle nature with a high elastic limit makes zirconia suitable for compression loading. Normally, zirconia is not recommended for constructing bridges. With improvements in fracture toughness, zirconia is being used to make bridges, but these require a larger cross section for connectors. Co-Cr alloys for RPDs have the highest elastic modulus and can retain adequate rigidity with less bulk of material. Tensile-strength values may not be meaningful because the framework will fail to function as soon as it is plastically deformed. The 5% ductility of Co-Cr alloy shown in **Figure 4-19** means that if the retentive clasp is made of this alloy, the ductility should allow a few adjustments of the clasp. Type IV gold has an elastic modulus high enough to resist flexing of FDPs made from this material. The high yield strength is good for preventing plastic deformation but may prove disadvantageous if one needs to burnish the margin. Solid-state transformation can be used (**Chapter 2, Solid-State Reactions in High Noble and Noble Alloy Systems**) to soften the alloy, making the process of burnishing the margins easier. The process of age hardening will bring the alloy back to a higher elastic modulus and

high yield strength for normal use. The hardness of the material usually increases along with the elastic modulus. These alloys have elastic moduli 3 to 7 times that of the enamel ($E = 33.6$ GPa). One should consider the impact of the potential hardness of the metal on the opposing restoration or tooth structure.

The right plot in **Figure 4-19** shows one denture resin and two composites. The computer-aided design/computer-aided manufacturing (CAD-CAM) block in this diagram is a highly filled composite designed for digital milling. In the discussion regarding stress concentration, the use of restorative materials of similar elastic modulus to that of the tooth was noted as desirable. The elastic moduli of both the resin and composite materials are between those of enamel and dentine. Some composites have elastic moduli as low as that of the denture resin shown in **Figure 4-19**. Because they have elastic moduli lower than that of enamel, they are not likely to induce excessive wear on the natural dentition. Denture resin has the lowest elastic modulus with the highest flexibility. Denture bases are not bound in a limited space like tooth cavity preparations. They are resting on soft tissue and may flex more than fixed restorations. Greater flexibility allows them to flex without the risk of fracture. The mechanical properties of these restorative materials and how their properties are used will be discussed in the respective chapters.

The magnitude of mastication forces is unknown for individual patients, to the extent that the dentist cannot estimate the stresses that will be induced in dental restorations. However, patients who exhibit evidence of extreme bruxism represent a higher-risk population for the fracture of brittle restorative materials. The

knowledge of the relationships between the properties of restorative materials known to exhibit excellent long-term survival performance is constantly reinforced by clinical experience. As is true for the field of engineering, the dental profession is aware that the best test of a successful restorative material is the test of time under actual clinical conditions.

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Davis JR (Ed): *Metals Handbook, Desk Edition*, Metals Park, OH, 1998, ASM International.

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This classic textbook on fracture surface analysis provides an excellent overview of fractographic techniques. Since many dental materials are brittle in nature, the identification of fracture patterns and the crack origin are useful to identify the principal sites of crack initiation.

Griffith AA: The phenomena of rupture and flow in solids, *Philos Trans Royal Soc A* 221:163–198, 1920.

Griffith proposed that minute cracks in a general glass act as a stress raiser that reduces the theoretical strength of glass to 1% of that predicted for its theoretical strength. He also concluded that the magnitude of the fracture stress and the square root of the critical flaw depth was a constant.

Acknowledgment

The author wishes to acknowledge Dr. Kenneth J. Anusavice for his contribution to the earlier editions of this chapter.

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Based on the shortcomings of Griffith's theory for ductile materials, Irwin modified Griffith's equations by accounting for inelastic behavior at the crack tips.

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5

Resin-Based Composites

OUTLINE

History of Composites

Composition and Function

Classification of Dental Composites

Properties of Resin-Based Composites

Finishing and Polishing of Composites

Repair of Composites

Composite-Based Indirect Restorations

Selection Criteria for Posterior Composites

Photocuring Training, Evaluation, and Process Management

KEY TERMS

Activation Process by which sufficient energy is provided to induce an initiator to generate free radicals and cause polymerization to begin.

Activator Source of energy used to activate an initiator and produce free radicals; the source of energy can be an electron-donating chemical, light, and/or heat.

C-factor Configuration factor. This represents the ratio between the bonded surface area of a resin-based composite restoration and the nonbonded or free surface area. The greater the C-factor, the greater the stress that develops at the restoration margin, which can lead to gap formation, marginal breakdown and leakage, and other problems (e.g., secondary caries).

Chemical-activated/self-cured/resin/composite Composite system consisting of two pastes—one containing an initiator and the other an activator—which, when mixed together, release free radicals that initiate polymerization. Many terms have been used throughout the development of this material; we will use either *chemical-activated* or *self-cured* in this book.

Coupling agent A compound that provides chemical bonds between two dissimilar classes of materials. For example, organosilane compounds are applied to the surfaces of silicate-based fillers to ensure that they are chemically bonded to the resin matrix of a dental composite.

Degree of conversion (DC) Percentage of carbon–carbon double bonds ($-C=C-$) converted to single bonds ($-C-C-$) during curing to form a polymeric resin. Also known as *degree of cure* and *degree of monomer-to-polymer conversion*.

Dental composite Highly crosslinked polymeric materials reinforced by a dispersion of amorphous silica, glass, crystalline, mineral, or organic resin filler particles and/or short fibers bonded to the matrix by a coupling agent. In dentistry, it is often called just “composite.”

Depth of cure Depth or thickness of a light-cured resin that has attained adequate mechanical strength from polymerization when exposed to a light source under a specific set of conditions.

Dual-cured resin Dental composite that contains both chemical-activated and light-activated components to initiate

polymerization and potentially overcome the limitations of either the chemical- or light-cured system when used alone.

Filler Inorganic, glass, and/or organic-resin particles that are dispersed in a resin matrix to increase rigidity, strength, and wear resistance and to decrease thermal expansion, water sorption, and polymerization shrinkage. Radiopaque fillers can also be added to impart radiopacity to dental composites. Alumino-fluorosilicate fillers can be added to release fluoride from dental composites.

Flowable composite Hybrid composite with reduced filler level and a narrower particle-size distribution to increase flow and promote intimate adaptation to prepared tooth surfaces. Flowable composites are often used as the first layer of a cavity filling to improve filling adaptation to the cavity.

Free radical An atom or group of atoms (R) with an unpaired electron (\cdot). R-producing reactions initiate and propagate polymerization and eventually lead to a final set.

Gel point/gelation The point in the polymerization reaction where sufficient crosslinks have formed to produce a rigid, glassy state in which internal flow among the developing polymer chains has stopped. All but localized molecular motion has stopped. After the gel point, stresses cannot be relieved but instead continue to increase and concentrate near the bonded interfaces. Thus, reducing the polymerization rate provides more time for adjacent polymer chain segments to slip among themselves to lower-energy configurations and relieve developing stresses before the polymerization reaches gel point.

Inhibitor A chemical added to resin systems to minimize spontaneous polymerization to extend the storage life of the resin through free radical-scavenging mechanisms. It also increases the working time of self-cured resin composites.

Initiator A free radical-forming chemical used to start the polymerization reaction. It enters into the chemical reaction and becomes part of the final polymer compound; thus it is not a catalyst, although it is often incorrectly labeled as such.

Light-cured/light-activated resin/composite Resin or particle-filled resin consisting of a single component that becomes polymerized through the use of a photosensitive initiator system

(typically camphorquinone and an amine) and a light-source activator (typically visible blue light). *Photocured* and *photoinitiated* are also used in the literature; we will use either *light-activated* or *light-cured* in this book.

Matrix A plastic resin material that forms a continuous phase upon curing and binds the reinforcing filler particles.

Oxygen-inhibited layer The thin surface region of a polymerized resin containing unreacted methacrylate groups arising from dissolved oxygen, which acts to inhibit the free radical polymerization curing reaction; also known as the *air-inhibited layer*.

Resin Blend of monomers and/or macromolecules with other components that form a material with a set of useful properties.

The gold standard of reference for restorative filling materials is amalgam. However, amalgam has its own disadvantages, such as (1) poor esthetics, (2) unfounded concerns about health hazards from the leakage of mercury, and (3) waste-disposal concerns. Because resin-based composites can be made to match the natural appearance of teeth, they have become the most popular of the esthetic or tooth-colored filling materials and are widely used for a variety of dental applications.

Another key advantage of resin materials is that they can be made in a range of consistencies, from highly fluid to rigid pastes, which allows them to be conveniently manipulated and molded to a custom-made form, and then converted through a polymerization *curing* reaction to a hard, strong, attractive, and durable solid.

History of Composites

During the first half of the 20th century, silicates were the tooth-colored material of choice for cavity restoration. Silicates release fluoride and are excellent for preventing caries, but they become severely eroded within a few years. Acrylic resins, which are based on polymethylmethacrylate (PMMA), soon replaced silicates for their tooth-like appearance, insolubility in oral fluids, ease of manipulation, and low cost. Unfortunately, these acrylic resins had relatively poor wear resistance and tended to shrink severely during setting, which caused them to pull away from the cavity walls, thereby producing crevices or gaps that facilitate leakage within these gaps. In addition, thermal expansion and contraction caused further stresses to develop at the cavity margins when hot or cold beverages and foods were consumed.

These problems were reduced somewhat by incorporating quartz particles in the resin. The **filler** does not take part in the setting reaction but occupies space that reduces the number of reactions taking place and the corresponding shrinkage. In addition, commonly used fillers have a low coefficient of thermal expansion. However, these filler-reinforced PMMA resins were not very successful, in part because the fillers do not bond chemically to the resin. Thus defects developed between the fillers and the surrounding resin and led to leakage, staining, and poor wear resistance.

In 1962, Bowen developed a new type of composite material that largely overcame these problems. Bowen's main innovations were bisphenol-A glycidyl dimethacrylate (*bis*-GMA), a monomer that forms a crosslinked matrix that is highly durable, and a surface treatment using an organic silane compound called a *coupling agent* to bond the filler particles to the resin matrix. Current tooth-colored restorative materials continue to use this technology, but many further innovations have been introduced since then.

In the late 1960s, a category now known as *traditional composites* (also known as *conventional* or *macrofill composites*) was developed; this contained very large particles of ground amorphous silica and quartz, which imparted significant improvements in mechanical properties, water sorption, polymerization

shrinkage, radiopacity, and thermal expansion compared with unfilled acrylic. However, these composites suffered from roughening of the surface as a result of the selective abrasion of the softer resin matrix surrounding the harder filler particles and were not very esthetic. To improve surface smoothness and retain or improve the physical and mechanical properties of traditional composites, small-particle-filled composites were developed using inorganic fillers ground to a size range of about 0.5 to 3 μm but with a broad size distribution allowing a higher filler loading (80% to 90% by weight or 65% to 77% by volume). This resulted not only in smoother surfaces but also greater wear resistance and some decrease in polymerization shrinkage. Further advances in the filler component have resulted in microfill composites and nanocomposites, hybrid composites, and packable and flowable composites, just to name a few.

Other advances with the monomer component provide better chemical and mechanical properties, reduced shrinkage, color and storage stability, biocompatibility, and other features. Today, resin matrix-forming monomers in composite resins are highly complex and use a variety of monomers and monomer blends of various molecular weights and functions.

Finally, advances in curing technology have yielded **light-cured** systems that make curing resins on demand possible and improve working time and ease of manipulation. Initially an ultraviolet (UV) curing system was used, but this system had several drawbacks and was soon replaced by visible blue-light curing systems. These advances were soon followed by further developments in curing-lamp technology, going from tungsten light bulbs to light-emitting diodes (LEDs).

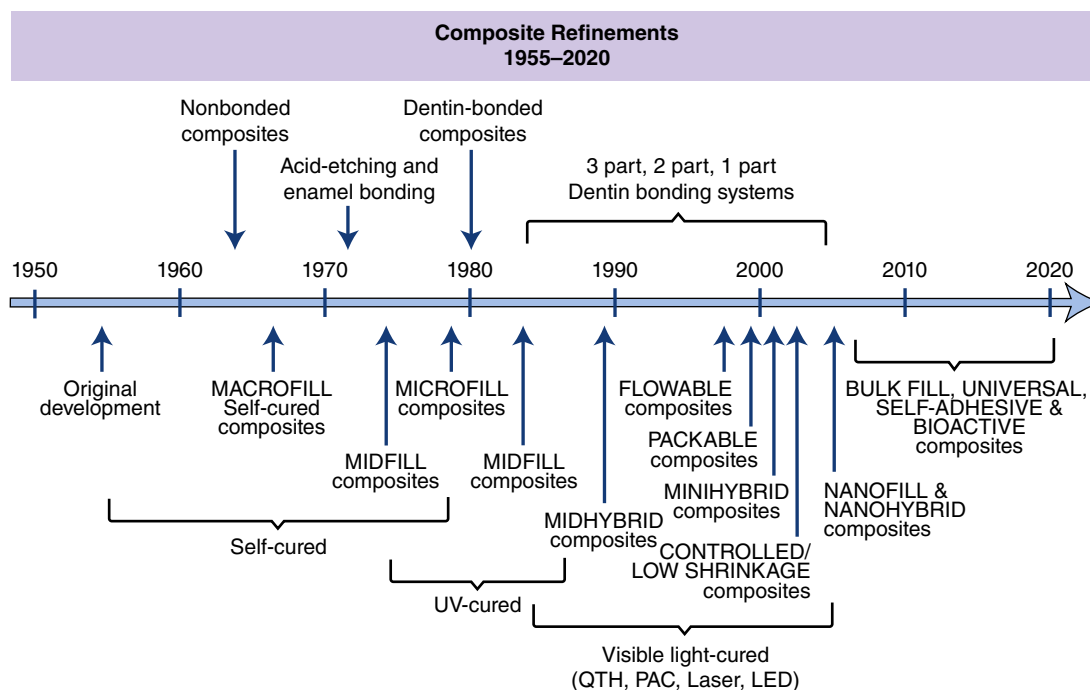
Figure 5-1 illustrates the history of and achievements in **dental composites**.

CRITICAL QUESTION

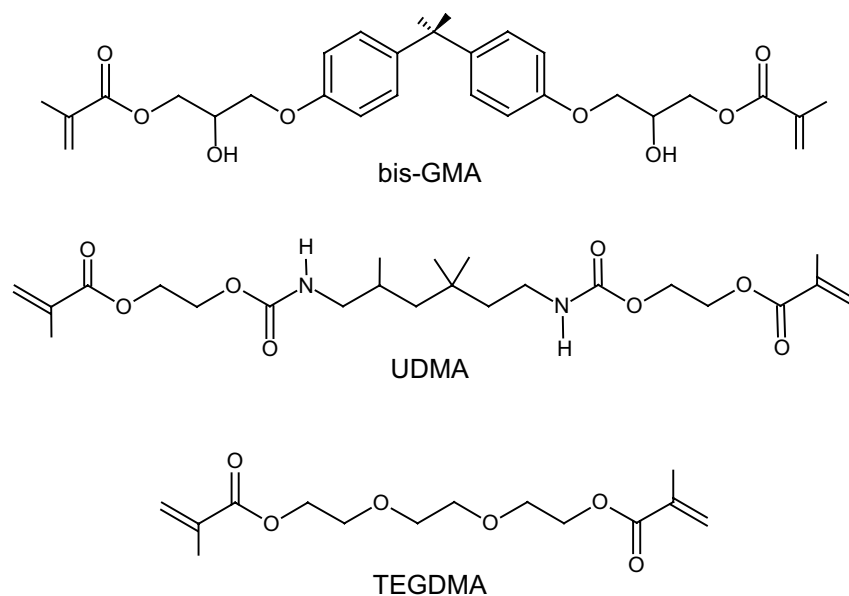
What are the three essential components of resin composite materials?

Composition and Function

Dental composites are made up of three major components: a highly crosslinked polymeric resin matrix; a dispersion of glass, silica, crystalline, metal oxide, resin-reinforcing particles, short fibers, or their combinations as filler; and a coupling agent bonding filler to the matrix. In addition, there is an activator-initiator system that converts the soft, moldable filling material to a hard, durable restoration, and there are combinations of pigments to match the color of tooth structure. Other additives include UV absorbers to improve color stability; inhibitors to extend storage life and increase working time for chemical-activated resins; and components to enhance performance, appearance, and durability.



• **Figure 5-1** Chronology of dental composite developments in monomer, filler, bonding, and curing technologies. *LED*, Light-emitting diodes; *QTH*, quartz-tungsten-halogen. (Adapted from Bayne SC: Dental biomaterials: where are we and where are we going? *J Dent Educ* 69:571–585, 2005.)



• **Figure 5-2** Chemical structure of bisphenol A glycidyl dimethacrylate (*bis*-GMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA).

CRITICAL QUESTIONS

What roles do *bis*-GMA and other high-molecular-weight dimethacrylate monomers play in the function and performance of dental resins?
Why are diluent monomers used, and what are the tradeoffs for their use?

Matrix

The resin matrix in most dental composites is based on a blend of aromatic and/or aliphatic *dimethacrylate* monomers such as bisphenol A glycidyl methacrylate (*bis*-GMA) and urethane

dimethacrylate (UDMA) (Figure 5-2) that form crosslinked, strong, rigid, and durable polymer structures. Note that the methacrylate groups are found at the ends of the chain or at the end of branching chains. *Bis*-GMA resin is a dimethacrylate of aromatic esters synthesized from an epoxy resin of ethylene glycol of *bis*-phenol A and methyl methacrylate. The two –OH groups of this material forming hydrogen bonds between the monomers make it extremely viscous. The rigid core of two aromatic groups limits the ability of *bis*-GMA molecules to rotate efficiently to participate in the polymerization process that often leaves one of the two

methacrylate groups unpolymerized. This results in one end of a *bis*-GMA becoming part of a polymer chain and the rest of the molecule becoming a methacrylate terminated pendant group. The efficiency of polymerization and crosslinking is expressed by the percentage of reacted (converted) methacrylate groups after polymerization and is known as the **degree of conversion (DC)**.

Various dimethacrylate resin combinations have been explored through the years in attempts to reduce viscosity and increase the DC. The UDMA's have shown particular promise. UDMA resins are any monomer containing one or more urethane groups ($-\text{NH}-\text{CO}-\text{O}-$) and two methacrylate end groups (Figure 5-2).

Because of the large molecular volume of these monomers, polymerization shrinkage can be as low as 0.9% (average of 1.5% compared with a range of 2% to 3% for most composites) when combined with inorganic particulate fillers at levels of up to 88% by weight. UDMA (about 20 Pa·s) and *bis*-GMA (about 800 Pa·s, similar to honey on a cold day) are highly viscous and are difficult to blend and manipulate. Thus varying proportions of lower-molecular-weight highly fluid monomers such as triethylene glycol dimethacrylate (TEGDMA; 0.005 to 0.05 Pa·s; Figure 5-2) and other lower-molecular-weight dimethacrylates to blend with and dilute the viscous components to attain resin pastes sufficiently fluid for clinical manipulation and for incorporating enough filler to reinforce the cured resin are necessary. For example, a blend of 75% *bis*-GMA and 25% TEGDMA by weight has a viscosity of about 4.3 Pa·s, whereas the viscosity of a 50% *bis*-GMA/50% TEGDMA blend is about 0.2 Pa·s (similar to thin syrup). Unfortunately, these smaller, diluent monomers undergo greater polymerization shrinkage that generates more shrinkage stress, which may cause the formation of marginal gaps and increase the risk of eventual leakage and the problems that may result, partially offsetting the advantage of using large monomers such as *bis*-GMA.

CRITICAL QUESTIONS

What roles do the fillers play in the function and performance of dental resins?

Filler

Incorporation of fillers, generally between 30% and 70% by volume or 50% and 85% by weight, has transformed resins into functional materials that withstand the chemical, physical, and mechanical challenges of the oral environment. In this section, we will discuss the function of fillers in composites, the required properties, and types of fillers.

Function of Fillers

Fillers can provide the following benefits:

- **Reduction of polymerization shrinkage/contraction.** Although shrinkage varies from one commercial composite to another, it typically ranges from slightly less than 1% up to about 4% by volume.
- **Reduction in thermal expansion and contraction.** As the overall expansion coefficient decreases with filler loading and approaches that of tooth tissue, less interfacial stress is produced because of differential volumetric changes while an individual consumes hot and cold foods and beverages.
- **Decreased water sorption.** Absorbed water softens the resin and makes it more prone to abrasive wear and staining.

- **Reinforcement.** As the volume fraction of filler approaches approximately 70%, abrasion and fracture resistance are raised to levels approaching those of tooth tissue, thereby increasing both clinical performance and durability.
- **Control of workability/viscosity.** Filler loading, filler size, and the range of particle sizes and shapes all markedly affect the consistency and clinical manipulation of a composite paste. Consistency and manipulation properties determine the ease of operation, the skill and time required, and also how reliably a cavity can be restored free of errors and with the proper interproximal contact, occlusal anatomy, smoothness, and appearance.
- **Imparting radiopacity.** Leaking margins, secondary caries, poor proximal contacts, wear of proximal surfaces, and other problems cannot be detected adjacent to inherently radiolucent resins. Radiopacity is most often imparted by adding radiopaque inorganic compounds such as glass filler particles with heavy-metal atoms, such as barium (Ba), lanthanum (La), strontium (Sr), ytterbium (Yb), zinc (Zn), or zirconium (Zr). For optimal diagnostic contrast, the restoration should have a radiopacity approximately equal to that of enamel, which is about twice that of dentin. Exceeding the radiopacity of enamel by a large degree will have the effect of obscuring radiolucent areas caused by gap formation or secondary caries.
- **Fluoride release.** Ytterbium fluoride (YbF_3) and aluminofluorosilicate glass (traditionally used in glass ionomers) are able to release fluoride from dental composites.

CRITICAL QUESTION

Why is there a tradeoff among workability, durability, and esthetics when fillers are incorporated in resins?

Characteristics of Fillers

In the early versions of dental composites, quartz had been used extensively as a filler because this material is chemically inert. Quartz is very hard, making the composite abrasive to opposing teeth or restorations and difficult to finish and polish to a smooth surface. So-called *amorphous silica* has the same composition and refractive index as quartz; however, silica is not crystalline and not as hard, thus greatly reducing the abrasiveness of the composite surface structure and improving its polishability.

The most commonly used glass filler is Ba glass. Although Ba glass fillers also provide radiopacity, they are not as inert as quartz or amorphous silica and are slowly leached and weakened in acidic liquids such as citrus juices, high-pH solutions, and other oral fluids. The glass filler is also attacked over time by caries-protective acidulated phosphate fluoride solutions or gels. Because of the differences in the composition of saliva among patients, the clinical effects of exposure to saliva are difficult to predict. However, the implication is that glass-filled composites will gradually become more susceptible to abrasive wear, and hence they will have a shorter functional lifetime compared with silica-reinforced resins.

For acceptable esthetics, the translucency of a composite restoration must be similar to that of tooth structure. Thus the refractive index of the filler must closely match that of the resin. For *bis*-GMA and TEGDMA, the refractive indices are approximately 1.55 and 1.46, respectively, and a mixture of the two components in equal proportions by weight yields a refractive index of approximately 1.50. Most of the glasses and quartz used for fillers have refractive indices of approximately 1.50, which is adequate for sufficient translucency.

Increasing filler loading improves the most important properties discussed so far; however, there is a limit of loading. For example, if the particle size were uniform spheres, no matter how tightly packed the spheres are, as illustrated in the crystalline structure shown in Chapter 2, *Crystalline Structure*, the maximal theoretical packing fraction for close-packed spherical structures of uniform size is approximately 74% by volume. However, smaller particles could still be inserted among the larger spheres. By extending this process, a continuous distribution of progressively smaller particles can yield a higher filler loading. Therefore a distribution of particle sizes is used to maximize the volume fraction of filler in composites.

Curing of composites produces an initially smooth, resin-rich surface, but finishing operations remove the resin matrix from the perimeter of filler particles, exposing particles that protrude from the surface. Particles larger than the wavelength of visible light cause light scattering, which increases opacity and produces a visibly rough texture when the particles are exposed at the surface. A roughened surface also tends to accumulate stains and plaque. The traditional inorganic filler particles had average diameters of about 8 to 40 μm . Currently, particles range from 5 nm to 2 μm . The advantage of using small particles is that they improve esthetics (appearance) and smoothness to the tongue (polishability). Oral wear mechanisms complement this process, such that the ultimate smoothness that can be maintained is highly dependent on particle size.

However, the smaller the filler particle size, the higher the surface-to-volume ratio available to form polar or hydrogen bonds with monomer molecules to inhibit their flow and increase viscosity (resistance to mixing and manipulation). Thus less filler can be added. Therefore there is always a tradeoff among the requirements for workability, durability, and esthetics. The clinician's challenge is to make an informed judgment concerning the claims for the many products offered and to select one that is well suited to a particular clinical application.

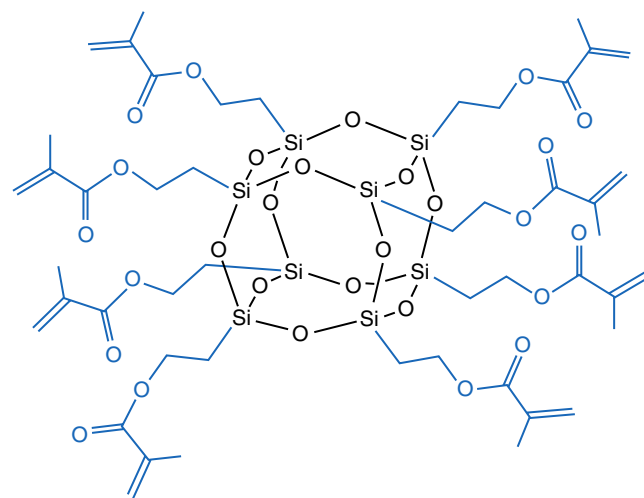
Types of Fillers

Various transparent mineral fillers are employed in formulating composite resins. These include so-called “soft glass” and borosilicate “hard glass”; fused quartz; aluminum silicate; lithium aluminum silicate (beta-eucryptite, which has a negative coefficient of thermal expansion); ytterbium fluoride; and barium, strontium, zirconium, and zinc glasses. More discussion on the particle size and fabrication of related fillers is provided later in the section on the classification of composites by filler particle size.

In the quest for improved aesthetics and, hence, smaller particle sizes, two filler systems, organically modified ceramics (ormocer) and polyhedral oligomeric silsesquioxane (POSS), in which a portion of the reinforcing component operates at molecular scale, have been introduced.

Ormocer

Ormocer is an acronym for *organically modified ceramics*. They are considered to be molecule-sized hybrid structures consisting of inorganic–organic copolymers. These molecular hybrids consist of, for example, methacrylate-terminated chains grafted onto a central cyclic polysiloxane 2- to 3-nm particle. These nanoparticles are dispersed on a molecular scale, and high-molecular-weight, flexible, relatively low-viscosity, crosslinkable molecules (“oligomers”) result. The large spacing between crosslinks resulting from curing produces a low level of polymerization shrinkage, and the inorganic network provides abrasion resistance through the glasslike structure and low water sorption resulting from hydrophobicity.



• **Figure 5-3** Methacryl polyhedral oligomeric silsesquioxane, a 12-sided silicate cage structure having polymerizable methacrylate pendant groups. (Courtesy Hybrid Plastics, Inc., Hattiesburg, MS.)

Ormocers are used in the formulation of several commercial composites (e.g., Definite and Admira, Voco GmbH, Cuxhaven, Germany; Ceram-X, Dentsply International, York, PA). Whereas the molecule-sized silicate particles provide some reinforcement, ground glass and/or other fillers are typically required for sufficient reinforcement. Therefore ormocer is often considered as part of the matrix of the composite. Advantages of ormocer-based dental materials include limited cure shrinkage, very high biocompatibility, good manipulation properties, and excellent esthetics.

POSS

POSS is an acronym for *polyhedral oligomeric silsesquioxane*. The molecules are 12-sided silicate cages produced from silane and functionalized to copolymerize with other monomers. A silsesquioxane is a chemical structure with the composition $R_n\text{Si}_n\text{O}_{1.5n}$, for example, $(\text{CH}_3)_8\text{Si}_8\text{O}_{12}$. For the POSS materials used in dental applications, the R-group is typically a methacrylate (Figure 5-3).

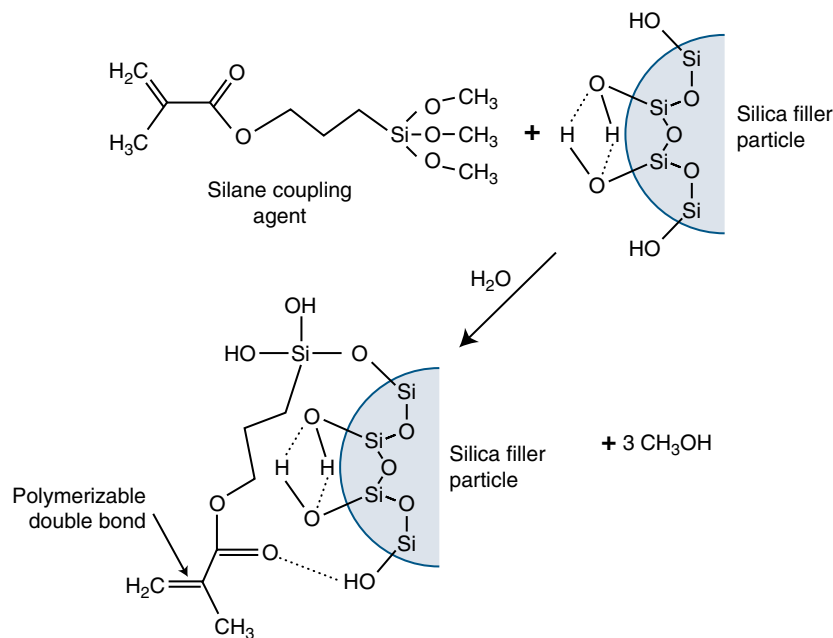
POSS is a molecule-sized hybrid organic–inorganic oligomeric compound that can disperse homogeneously in compatible monomers and become covalently incorporated into crosslinked networks upon curing. Like the ormocer-type materials, the silicate cage structures provide a reinforcing function, but filler particles must also be included to achieve the balance of mechanical and other properties required for adequate performance as dental composites. Depending on the dispersed filler, POSS-based resins are characterized as being highly polishable and having excellent polish retention, mechanical properties, and wear resistance. Current commercial products based on silsesquioxane technology include Artiste Nano-Hybrid Composite (Pentron Clinical, Wallingford, CT).

CRITICAL QUESTIONS

What roles do the coupling agents play in the function and performance of dental resins?

Coupling Agent

As stated previously, it is essential that filler particles be bonded to the resin matrix. This allows the more flexible polymer matrix to transfer stresses to the higher-modulus (more rigid and stiffer)



• **Figure 5-4** The chemical structure of γ -methacryloxypropyltrimethoxy silane and an idealized diagram of how a silane coupling agent is hydrolyzed and becomes attached to silica and glass filler particle surfaces. Such silanized particles are then reactive and can “couple” the particles to the resin matrix by copolymerization with the double bond in the silane propylmethacrylate group ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}-\text{C}_3\text{H}_6-\text{Si}-$). (Data taken from Söderholm K-J, Shang S-W: Molecular orientation of silane at the surface of colloidal silica. *J Dent Res* 72:1050–1054, 1993.)

filler particles. The chemical bond between the two phases of the composite is formed by a coupling agent, a difunctional surface-active compound that adheres to filler particle surfaces and also coreacts with the monomer forming the resin matrix. A properly applied coupling agent can impart improved physical and mechanical properties and inhibit leaching by preventing water from penetrating along the filler–resin interface.

Although titanates and zirconates can be used as coupling agents, organosilanes—such as γ -methacryloxypropyl trimethoxysilane—are used most commonly (Figure 5-4). In the presence of water, the methoxy groups ($-\text{OCH}_3$) are hydrolyzed to silanol ($-\text{Si}-\text{OH}$) groups, which can bond with other silanols on the filler surfaces by forming siloxane bonds ($-\text{Si}-\text{O}-\text{Si}-$). The organosilane methacrylate groups form covalent bonds with the resin when the resin is polymerized, thereby completing the coupling process. Proper coupling by means of organosilanes is extremely important to the clinical performance of resin-based composite restorative materials.

Inhibitors

Inhibitors are added to resin systems to minimize or prevent spontaneous or accidental polymerization of monomers. Inhibitors have a strong reactivity potential with **free radicals**. If a free radical is formed, for example, by brief exposure to room lighting when the material is dispensed, the inhibitor reacts with the free radical faster than the free radical can react with the monomer. This prevents the initiation of monomers and subsequent chain propagation. After all of the inhibitor is consumed, chain propagation can begin. A typical inhibitor is butylated hydroxytoluene (BHT), which is used in concentrations on the order of 0.01% by weight. Thus inhibitors have two functions: to extend the resin's storage life and to ensure sufficient working time.

Optical Modifiers

For a natural appearance, dental composites must have visual shading and translucency similar to the corresponding properties of tooth structure. Shading is achieved by adding various pigments usually consisting of minute amounts of metal oxide particles. Translucency and opacity are adjusted as necessary to simulate enamel and dentin. For example, if a class IV incisal area is reconstructed, the translucency of an unmodified composite might allow too much light to pass through the restoration. As a result, less light is reflected or scattered back to the observer, who perceives the incisal edge as too dark. This deficiency can be corrected by adding an opacifier. However, if an excessive amount of opacifier is added, too much light may be reflected, and the observer then perceives that the restoration is “too white,” or more correctly, “too high in value” (Chapter 3, **Three Dimensions of Color**). To increase the opacity, the manufacturer adds titanium dioxide and aluminum oxide to composites in minute amounts (0.001% to 0.007% by weight).

All optical modifiers affect light transmission through a composite. Thus darker shades and greater opacities have a decreased depth of light-curing ability and require either an increased exposure time or a thinner layer when cured. Studies have shown that for optimal polymerization, resins with darker shades and opacifiers should be placed in thinner layers. This consideration has added importance when a bonding agent covered by a composite layer is being cured.

Classification of Dental Composites

As the variety of dental composites increases in response to new innovations and needs, there are also several ways of classifying dental composites, depending on various aspects of the composites. A useful classification system for composites is one based on filler particle size and size distribution, as shown in Table 5-1. Dental composites can

TABLE 5-1 Classification of Resin-Based Composites and Indications for Use

Class of Composite	Particle Size and/or Unique Aspects of Filler Content	Clinical Use
Traditional (large particle, macrofill)	8- to 40- μ m glass or silica	High-stress areas
Homogeneous microfill	40-nm silica	Low-stress and subgingival areas that require a high luster and polish
Heterogeneous microfill (microfilled)	(1) 40-nm silica (2) larger prepolymerized organic resin particles containing 10–100 nm silica	Low-stress and subgingival areas where reduced shrinkage is essential
Nanofill	<100-nm silica or zirconia Homogeneous independent nanoparticles or nanoclusters	Anterior and noncontact posterior areas
Hybrid (large particle)	(1) 1- to 20- μ m glass (2) 40-nm silica	High-stress areas requiring improved polishability (classes I–IV)
Hybrid (midfiller)	(1) 0.1- to 10- μ m glass (2) 40-nm silica	High-stress areas requiring improved polishability (classes III, IV)
Hybrid (minifiller/SPF*)	(1) 0.1- to 2- μ m glass (2) 40-nm silica	Moderate-stress areas requiring optimal polishability (classes III, IV)
Nanohybrid	(1) 0.1- to 2- μ m glass or resin microparticles (2) \leq 100-nm nanoparticles	Moderate-stress areas requiring optimal polishability (classes III, IV)
Flowable/Injectable	Commercial composites made flowable, usually by lowering filler loading	Situations where improved flow is needed (e.g., a cavity base or liner, a sealant) or where access is difficult (class II)
Packable/Condensable	Increased loading of midfiller/minifiller hybrid with macrofillers; elongated, fibrous filler (100 μ m in length); and/or rough branched fillers	Situations where improved condensability is needed (classes I, II)
Bulk fill	Usually nanohybrids but also involves very high filler loadings to reduce polymerization shrinkage and/or stress. The refractive indices of the filler and monomer are also matched to increase composite translucency to allow increased light penetration and allow polymerization at greater depths.	Large posterior cavity preparations > 4 mm in depth
Universal	Usually nanohybrids but could be nanofills (or nanofills with prepolymerized particles)	Classes I–V

SPF, small-particle filled.

also be classified based on curing method, manipulation characteristics, application, unique characteristics, and any combination of these, as discussed in the following sections.

CRITICAL QUESTION

What are the similarities and differences in the mechanisms involved in chemical-activated and light-activated dental resins?

Classification by Curing Method

Methacrylate-functionalized monomers polymerize by the addition polymerization mechanism (also known as *chain-growth polymerization*) initiated by free radicals. Free radicals can be generated by chemical **activation** or by external energy activation (heat, light, or microwave). Because dental composites for direct placement use chemical activation, light activation, or a combination of the two, only these systems are discussed here.

Chemical-Activated (Self-Cured) Resins

Chemical-activated resins are supplied as two pastes, one of which contains the benzoyl peroxide initiator, and the other contains monomers and an aromatic tertiary amine activator (e.g., N,N-dimethyl-p-toluidine). When the two pastes are mixed together, the amine activates the benzoyl peroxide to form free radicals, and addition polymerization is initiated. There are inherent limitations with chemical activation. First, air is incorporated during mixing, leading to the formation of pores that weaken the structure and trap oxygen, which inhibits polymerization on the inner surfaces of the pores.

Second, the operator has no control over the working time after the two components have been mixed. Therefore both insertion and contouring must be completed quickly once the resin components are mixed. Thus today, they are mainly used for restorations and large foundation structures (buildups) that are not readily cured with a light source.

Third, the reactivity of oxygen to a radical is much higher than that of a monomer inhibiting polymerization on the

• Box 5-1 Advantages and Disadvantages of Chemical-Activated (Self-Cured) Resins

Advantages

Convenience and simplicity: no equipment needed, hazard-free
 Long-term storage stability
 Manipulation of working/setting time by varying proportions
 Degree of cure equal throughout material if mixed properly
 Marginal stress buildup during curing is much lower than for light-cured resins because of relatively slower rates of crosslink formation.

Disadvantages

Mixing causes air entrapment, leading to porosity that weakens the material and increases susceptibility to staining. This has been reduced by the use of mixing syringes.
 Aromatic amine accelerators oxidize and turn yellow with time (i.e., color instability).
 Difficult to mix evenly, causing unequal degree of cure and, consequently, poor mechanical properties

surface. During the inhibition period, this oxygen diffuses into the resin and is consumed by the radicals formed. This reaction forms an **oxygen-inhibited layer**. The thickness of the oxygen-inhibited layer is dependent on the viscosity of the resin, the solubility of oxygen in the monomer, and the initiating system used.

Fourth, self-cured resins tend to have initial yellow off-color and lower color stability as a result of the aromatic amine. This is another reason self-cured resins are not used as direct restorations.

Box 5-1 lists the advantages and disadvantages of chemical-activated resins.

Light-Activated (Light-Cured) Resins

To overcome the problems associated with chemical activation, systems using a photosensitive initiator system and a light source for activation were developed. The first light-activated systems were formulated for UV light, which has been replaced by visible blue-light-activated systems, with great improvements in the quality of the cured composites (Box 5-2). Light-curable dental composites are supplied as a single paste contained in a lightproof syringe or capsule because there is no chemical activator in the material. The free radical-initiating system, consisting of a photosensitizer and an amine co-initiator, is contained in this paste. As long as these two components are not exposed to light, they do not interact. However, exposure to light in the blue region (wavelength of about 468 nm) produces an excited state of the photosensitizer, which then interacts with the amine to form free radicals that initiate addition polymerization (Figure 5-5). Camphorquinone (CQ) is a commonly used photosensitizer that absorbs blue light with wavelengths between 400 and 500 nm. Only small quantities of CQ are required (0.2% by weight or less in the paste). A number of amine initiators are suitable for interaction with CQ, such as dimethylaminoethyl methacrylate (DMAEMA), which is also present at low levels of about 0.15% by weight.

In addition to avoiding the porosity of chemical-activated resins, light-activated materials allow the operator to complete insertion and contouring before curing is initiated. Furthermore, once curing is initiated, an exposure time of 40 s or less is required to light-cure a 2-mm-thick layer, compared with several minutes for

• Box 5-2 Advantages and Disadvantages of Light-Activated (Light-Cured) Resins

Advantages

No mixing needed, thus low porosity, less staining, stronger
 No aromatic amine accelerator, thus greatly improved color stability
 “Command” setting (upon exposure to an intense blue light). This means that working time is controlled, at will, by the clinician.
 Small increments of composite can be polymerized at a time, allowing the use of multiple shades within a single restoration and accommodating for shrinkage within each increment as opposed to bulk shrinkage.

Disadvantages

Limited cure depth: necessary to build up in layers of about 2 mm
 The marginal stress buildup during curing is much higher than in self-cured resins. This is a result of faster crosslinking, and thus reduced time for chains to slide among themselves and relax interfacial stress buildup resulting from cure shrinkage.
 Mildly sensitive to normal room illumination (thus, a crust will form when exposed too long to an examination light)
 A special lamp is needed to initiate curing.
 Poor lamp accessibility in posterior and interproximal areas; requires extra exposure time and care in placement and maintaining lamp tip angle and distance for optimal results
 Darker shades require longer exposure times.
 Cure is affected by additives such as ultraviolet absorbers for color stabilization, fluorescent dyes for clinical aesthetics, or excessive inhibitor concentration. They all absorb light or prevent reaction.
 Problems with lamps include the following:
 Glare is harmful to clinic personnel; use protective glasses or filters.
 Except for light-emitting diode (LED) lamps, curing light generates substantial heat and will cause pain at 2 to 3 mm in about 20 sec.
 Quartz-tungsten-halogen (QTH) bulbs dim with age; therefore, use proper instrumentation to monitor output irradiance.
 The lamp wavelength must be matched with the resin photoinitiation system.
 The irradiance of the light decreases with distance to the log scale.
 The curing angle is critical; maximal irradiance is delivered perpendicular (90°) to the resin surface.
 Training is required to develop best-practice techniques for optimum intraoral exposure to maximize the degree of cure.
 Incomplete curing owing to the previously described problems with lamps.

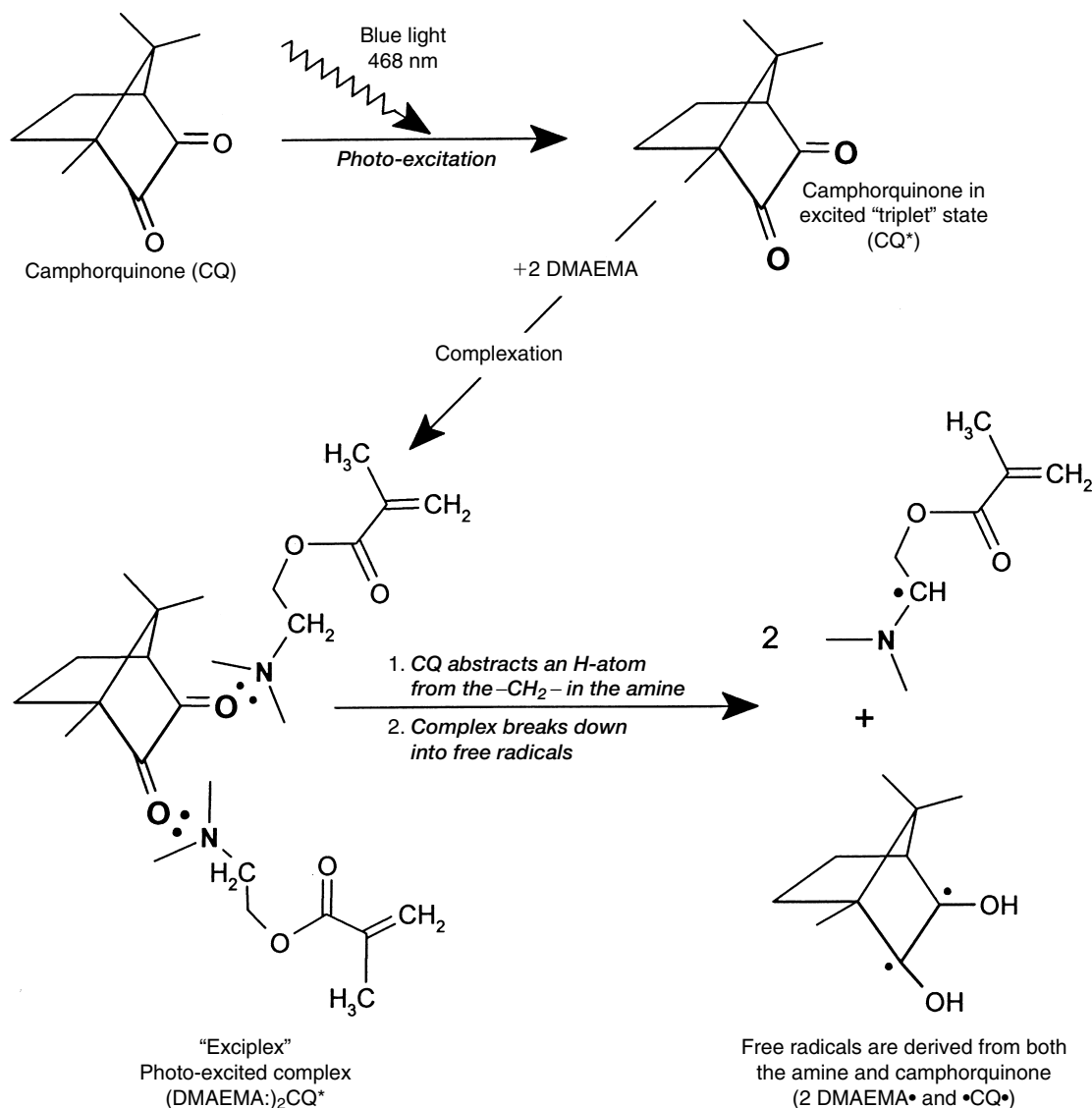
self-cured materials. Finally, light-cured systems are not as sensitive to oxygen inhibition as are the self-cured systems. Because of these advantages, visible light-activated composites are more widely used than chemical-activated materials.

However, light-cured composites have inherent limitations. For example, they must be placed incrementally when the bulk exceeds approximately 2 to 3 mm because of the limited depth of light penetration. Thus light-cured composites can actually require more time when making large restorations (e.g., in class II cavity preparations). The **depth of cure** has been raised to at least 4 mm with the development of bulk-fill composites (see Bulk-Fill Composites section). Other issues are related to the light-curing unit and are discussed in three areas: the curing lamps, the depth of cure, and the safety precautions for using lamps.

Box 5-2 lists the advantages and disadvantages of light-activated resins.

CRITICAL QUESTION

What are the tradeoffs among the several types of light sources used to photoactivate dental restorative resins?



• **Figure 5-5** The light-cured process is activated when a diketone photosensitizer, such as camphorquinone (CQ) absorbs a quantum of blue light and forms an excited-state complex (exciplex) with an electron donor such as an amine (e.g., dimethylaminoethyl methacrylate). In the figure, "••" denotes the unshared pair of electrons "donated" by the amines to the > C = O (ketone) groups in CQ. While in this activated complex, CQ extracts a hydrogen atom from the α -carbon adjacent to the amine group, and the complex decomposes into amine and CQ free radicals. The CQ free radical is readily inactivated. Thus in photoinitiation, only the amine free radicals act to initiate the addition polymerization reaction.

Curing Lamps

The two main types of lamps currently used for photoinitiation of the polymerization process are quartz-tungsten-halogen (QTH) lamps and LED lamps, with LED lamps quickly overtaking QTH lamps in popularity.

QTH or halogen lamps have a quartz bulb with a tungsten filament that irradiates both UV and white light, which must be filtered to remove heat and all wavelengths except those in the violet-blue range (about 400 to 500 nm) to match the photoabsorption range of CQ. The irradiance of the bulb (200 to 400 mW/cm²) diminishes with use, so a calibration meter is required to measure the irradiance.

LED lamps use a solid-state electronic process to emit radiation only in the blue part of the visible spectrum, between 440 and 480 nm,

and do not require filters. LEDs require low wattage, can be battery-powered and cordless, generate very little heat, and are quiet because no cooling fan is needed. Initially, they produced similar irradiance as QTH lamps (200 to 400 mW/cm²), but the latest versions are more intense and use two or more LED units to both increase irradiance (>1000 mW/m²) and extend the wavelength range. As such, significantly less time is needed to cure the composite using LED lamps. Their light bulbs are also cheaper to replace (up to a third of the price of QTH light bulbs) and more reliable.

CRITICAL QUESTION

What are the benefits and drawbacks of increasing the irradiance of curing lamps?

Polymerization is initiated when a critical concentration of free radicals is formed. This requires that a particular number of photons be absorbed by the initiator system, which is directly related to the wavelength, irradiance, and time of exposure. For maximum curing, a radiant energy influx of approximately 16 J/cm^2 is required for a 2-mm-thick layer of resin. This can be delivered by a 40-s exposure to a lamp emitting 400 mW/cm^2 ($40 \text{ s} \times 400 \text{ mW/cm}^2 = 16,000 \text{ mJ/cm}^2$ or 16 J/cm^2). By the law of reciprocity, the same result can be produced by a 20-s exposure at 800 mW/cm^2 or an exposure of about 13 s with a 1200-mW/cm^2 lamp. Thus increasing the irradiance of the lamp increases the rate and degree of cure. However, research studies have shown that a longer-than-calculated time might be needed when higher-irradiance light is used. In addition, faster curing with higher-irradiance light sources can increase shrinkage stress, as discussed in the following section.

CRITICAL QUESTIONS

How does lamp irradiance affect the depth of cure?

What are the most important factors that affect the depth of cure for a lamp with a given irradiance?

Depth of Cure and Exposure Time

LED lamps with substantially increased irradiances ($>1000 \text{ mW/cm}^2$) have opened the possibility of reduced exposure times with a greater depth of cure. However, with conventional composites, light absorption and scattering in resin composites reduce the irradiance and DC exponentially with the depth of penetration. Irradiance can be reduced by a factor of 10 to 100 in a 2-mm-thick layer of composite. This reduces monomer conversion to an unacceptable level at depths greater than 2 to 3 mm. Thus the surface must be irradiated for a longer time to deliver sufficient energy well below the surface. Given the limits imposed by the light scattering and absorption inherent in current restorative resins, the tradeoffs are such that increased irradiance will allow either shorter curing times for a given depth of cure or an increased depth of cure for a given exposure time, but there is little advantage in attempting to achieve both simultaneously. The practical consequence is that the curing depth is limited to 2 to 3 mm unless excessively long exposure times are used, regardless of lamp irradiance.

Light attenuation can also vary considerably from one type of composite to another, depending, for example, on the opacity, filler size, filler concentration, and pigment shade (i.e., darker shades and/or more opaque resins require longer curing times). For these reasons, manufacturers usually recommend curing times based on a particular curing device for each shade and type of resin. These recommended times are typically the absolute minimum required. To maximize both the degree of polymerization and the long-term clinical durability, the clinician should adjust the exposure time and curing technique to the irradiance of the light source used. Light is also absorbed and scattered as it passes through tooth structure, especially dentin, thereby causing incomplete curing in such critical areas as proximal boxes. Therefore, when one attempts to polymerize the resin through tooth structure, the exposure time should be increased by a factor of 2 to 3 to compensate for the reduction in light irradiance.

CRITICAL QUESTIONS

What are the critical exposure techniques and lamp-maintenance practices required for optimal curing and ensuring maximal longevity of resin-based composite restorations?

For the halogen (QTH) lamps, light irradiance is particularly susceptible to aging of the light source. For all types, faulty orientation of the light tip and too great of a distance between the light tip and restoration will reduce light output. Several surveys have shown that the curing units in many dental offices worldwide do not deliver an adequate light output. The bulbs, LEDs, reflectors, and internal filters in dental light-curing units of all types have been shown to degrade with use. In addition, autoclaving, the use of disinfectant chemicals, or restorative material adhering to the light tip can dramatically reduce light output.

Consequently, the lamp's output irradiance should be checked regularly, and the operator should always place the light tip as close as possible perpendicular to the restorative material and maintain this distance and orientation throughout the exposure time. Studies reported in 2010 and 2011 by Price and colleagues concluded that specialized training in these technique-related details substantially improves the intraoral degree of monomer-to-polymer conversion that is obtained.

Safety Precautions for Using Curing Lamps

The light emitted by curing units can cause retinal damage if a person looks directly at the beam. Thus never look directly into the light tip and minimize observation of the reflected light for longer periods. Protective eyeglasses and various types of shields that filter the light are available for increased protection for both clinical personnel and patients.

Dual-Cured Resins

One way to overcome the limits on curing depth and some of the other problems associated with light curing is to combine chemical-curing and light-curing components in the same resin. **Dual-cured resins** consist of two light-curable pastes, one containing benzoyl peroxide and the other containing an aromatic tertiary amine accelerator. They are formulated to cure very slowly when mixed for the self-cured mechanism. The curing process is then accelerated on "command" via light curing. The chief advantage of this system is assurance of completion of cure throughout, even if light curing is inadequate. The major disadvantage is the porosity caused by the required mixing, but this has been greatly alleviated by the use of mixing syringes. There is also less color stability than with the light-cured resins as a result of the aromatic amine accelerators, but this is still better than the self-cured systems because the concentration of the accelerators is reduced compared with self-cured resins. Finally, as with the self-cured resins, oxygen inhibition and porosity are problems with dual-cured resins. Dual-cured materials are intended for any situation that does not allow sufficient light penetration to produce adequate monomer conversion—for example, cementation of bulky ceramic inlays. This technology has been incorporated into direct composites to develop bulk-fill composites with unlimited depth of cure. Examples include Parkell HyperFil, Apex Injectafil DC, and Coltene Fill-Up!.

Classification by Filler Particle Size

The classification of fillers by particle size is shown in [Table 5-2](#). In conjunction with the chronology of dental composite developments shown in [Figure 5-1](#), it can be seen that the distribution and average size of filler particles played a major role in the advancement of dental composites. As such, a classification of dental composites based on the filler particle size can be used ([Table 5-1](#)).

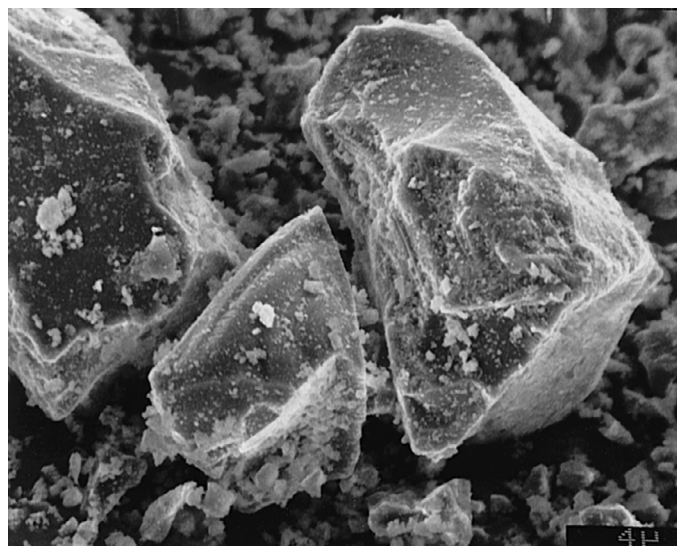
Traditional/Large-Particle/Macrophill Composites

These are the traditional composites with glass or silica macrofiller particles in the size range of between 8 to 40 μm (Figure 5-6). Because of their large particle size, these composites have lower relative viscosity and are easier to fill at higher loadings than microfills and nanofills. As such, they tend to be stronger and can be used in high-stress areas. However, the visibly rough texture after polishing, caused by the exposure of larger particles, has made this category of dental composite obsolete.

TABLE 5-2 Classification of Reinforcing Filler Particles by Size Range

Class of Filler	Particle Size
Macrofillers	10–100 μm
Midfillers	1–10 μm
Small/fine fillers	0.1–10 μm
Minifillers	0.1–1 μm
Microfillers	0.01–0.1 μm (agglomerated)
Nanofillers	0.005–0.1 μm^*

*5–100 nm, nonagglomerated.



• **Figure 5-6** Ground quartz filler particles with diameters of about 1 to 30 μm . Such relatively large fillers were used in early formulations of traditional composites. The smaller particles seen in the background contribute to a broad particle-size distribution. (Courtesy Dr. Karl-Johan Söderholm.)

Homogeneous Microfill Composites

The solution to rough surfaces and an opaque appearance was the homogeneous microfill composites, which used filler particles with a mean diameter much smaller than the wavelength of visible light. Such fillers are made by a pyrolytic precipitation process where a silicon compound such as SiCl_4 is burned in an oxygen/hydrogen atmosphere to form macromolecular chains of colloidal silica (see Figure 5-7), resulting in *amorphous silica* with an average size of 40 nm.

However, these particles, because of their extremely small size, have extremely large surface areas ranging from 50 to 400 m^2/g . In addition, the pyrolytic process results in particle “agglomeration” into long, molecular-scale chains (Figures 5-8 and 5-9). These nondiscrete, 3-D, chainlike networks drastically increase monomer viscosity and make clinical manipulation difficult. Thus filler incorporation at high enough loading to adequately reinforce the resin is difficult. In fact, when incorporated directly in “homogeneous” microfill composites, only about 2% by weight produces a stiff paste that is much too viscous for clinical manipulation (Figure 5-10). They are often just called *microfill composite*.

CRITICAL QUESTIONS

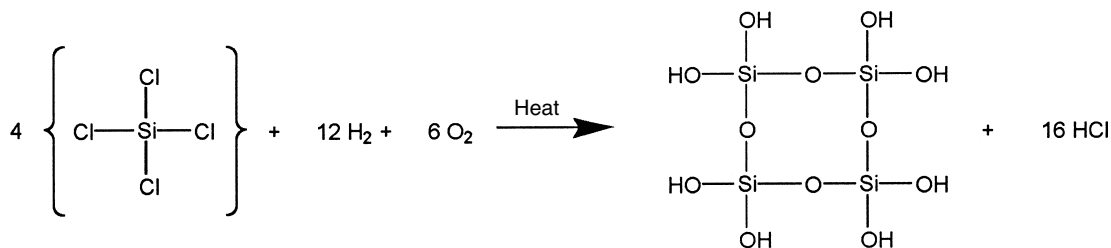
Why is the polymerization shrinkage of microfilled (heterogeneous microfill) composites not higher than that of conventional composites even though the inorganic filler loading in microfill is substantially lower?

Microfilled (Heterogeneous Microfill) Composites

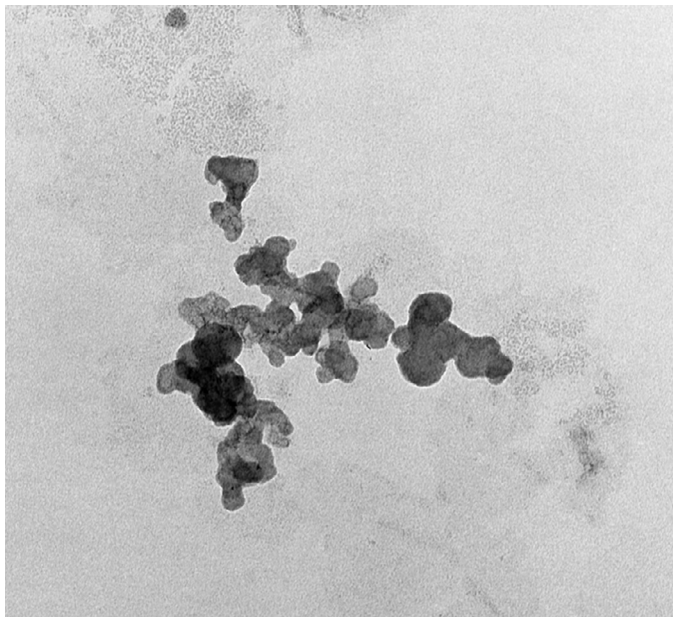
To increase the inorganic filler loading of microfill composites, a resin-based filler loaded with 10- to 100-nm inorganic colloidal silica is used instead. These resin-based, heterogeneous fillers are made by incorporating about 50 vol% of silane-treated colloidal silica microfiller into the monomer at a slightly elevated temperature to lower the viscosity and by using large industrial machines capable of mixing high-viscosity blends. The mixture is cured, and then pulverized to make a filled resin powder consisting of 5- to 50- μm particles. These amorphous colloidal silica-containing particles are then used as an “organic” filler, which is incorporated into the monomer with additional silane-treated colloidal silica to form a workable paste. In this way, the overall *inorganic* filler content of the final, cured composite is increased to about 50% by weight. However, if the composite particles are counted as filler particles, the filler content is closer to 80% by weight (approximately 60% by volume). A diagram representing the preparation of the filler in microfilled resins of this type is shown in Figure 5-11. This class of material is called *heterogeneous microfill* or *microfilled composite*.

CRITICAL QUESTIONS

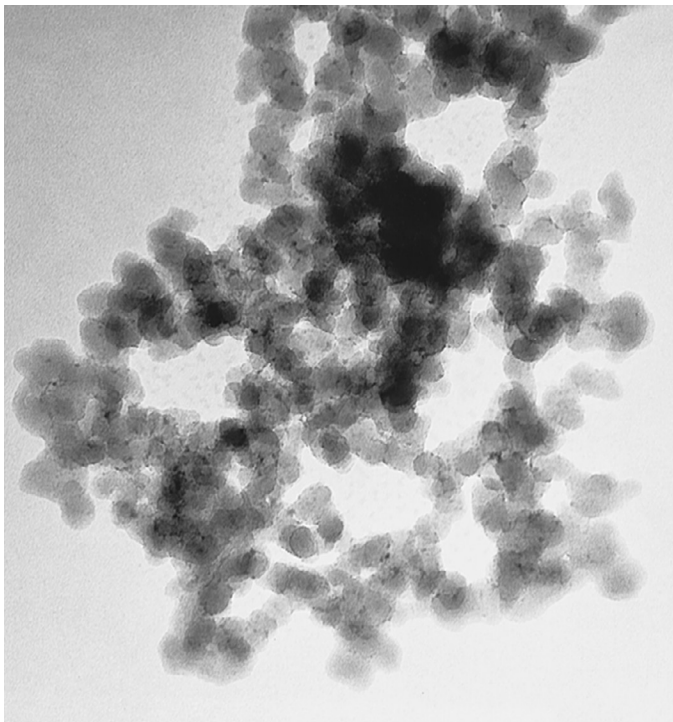
Which properties of microfilled resins are generally inferior to those of other resin-based composite materials, and what are the clinical implications of these deficiencies?



• **Figure 5-7** Pyrogenic reaction showing the initial formation of fumed silica particles in the 40-nm size range, as used in microfill resins. (Courtesy Dr. Karl-Johan Söderholm.)

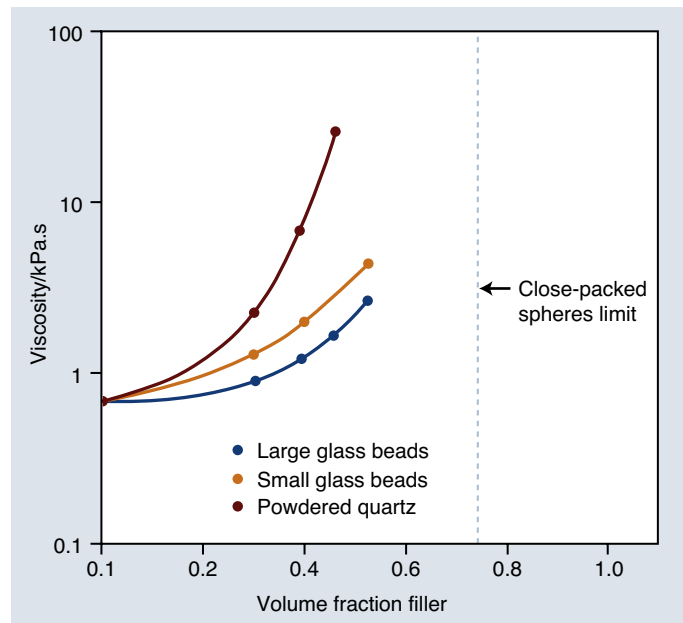


• **Figure 5-8** Transmission electron microscope image of fumed silica particles produced by the pyrogenic reaction shown in Figure 5-7. The particle diameters average approximately 40 nm. (Courtesy Dr. Karl-Johan Söderholm.)

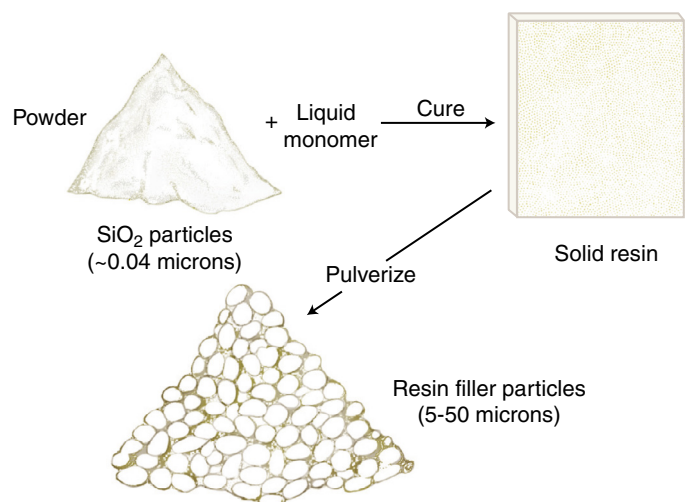


• **Figure 5-9** The pyrogenic silica used in microfill composites has a very large total surface area because of its extremely small average particle size of about 0.04 μm /40 nm. These particles agglomerate and form long chains, as seen in this transmission electron micrograph. (Courtesy Dr. Karl-Johan Söderholm.)

Whereas microfilled composites are among the more highly polishable restorative composites, their physical and mechanical properties are generally inferior to those of traditional composites. This is to be expected because 40% to 80% by volume of the restorative material is made up of resin, resulting in



• **Figure 5-10** The effect of filler specific surface area on the viscosity (log scale) of the uncured resin matrix. The smaller the particle, the larger is the surface area and the greater the viscosity buildup. (Adapted from Darvell BW: *Materials Science for Dentistry*, ed 10, Cambridge, UK, 2018, Woodhead Publishing Ltd.)



• **Figure 5-11** Preparation of resin filler particles for use in microfilled composites. The filler particles in a microfilled composite consist of pulverized "composite filler particles" dispersed in a cured resin matrix. Pyrogenic colloidal silica particles of about 0.04 μm (about 40 nm) are incorporated into both the precured resin filler particles and the curable monomer, with the precured resin containing a substantially higher concentration. (Modified from Lambrechts P: *Basic Properties of Dental Composites and Their Impact on Clinical Performance*. Thesis. Leuven, Belgium, Katholieke University, 1983.)

greater water sorption, a higher coefficient of thermal expansion, and decreased elastic modulus. In addition, the weak bond of the prepolymerized particles to the clinically cured resin matrix results in decreased tensile strength, similar to that of composites with nonsilanized filler particles. Table 5-3 shows various properties of different types of composites for reference.

TABLE 5-3 Properties of Composite Restorative Materials

Characteristic/ Property	Unfilled Acrylic	Traditional	Hybrid (Small Particle)	Hybrid (All- Purpose)	Microfilled	Flowable Hybrid	Packable Hybrid	Enamel	Dentin
Size (μm)	—	8–12	0.5–3	0.4–1.0	0.04–0.4	0.6–1.0	Fibrous	—	—
Inorganic filler (vol%)	0	60–70	65–77	60–65	20–59	30–55	48–67	—	—
Inorganic filler (wt%)	0	70–80	80–90	75–80	35–67	40–60	65–81	—	—
Compressive strength (MPa)	70	250–300	350–400	300–350	250–350	—	—	384	297
Tensile strength (MPa)	24	50–65	75–90	40–50	30–50	—	40–45	10	52
Elastic modulus (GPa)	2.4	8–15	15–20	11–15	3–6	4–8	3–13	84	18
Thermal expansion coefficient (ppm/ $^{\circ}\text{C}$)	92.8	25–35	19–26	30–40	50–60	—	—	—	—
Water sorption (mg/cm 2)	1.7	0.5–0.7	0.5–0.6	0.5–0.7	1.4–1.7	—	—	—	—
Knoop hardness (KHN)	15	55	50–60	50–60	25–35	—	—	350–430	68
Curing shrinkage (vol%)	8–10	—	2–3	2–3	2–3	3–5	2–3	—	—
Radiopacity (mm of Al)	0.1	2–3	2–3	2–4	0.5–2	1–4	2–3	2	1

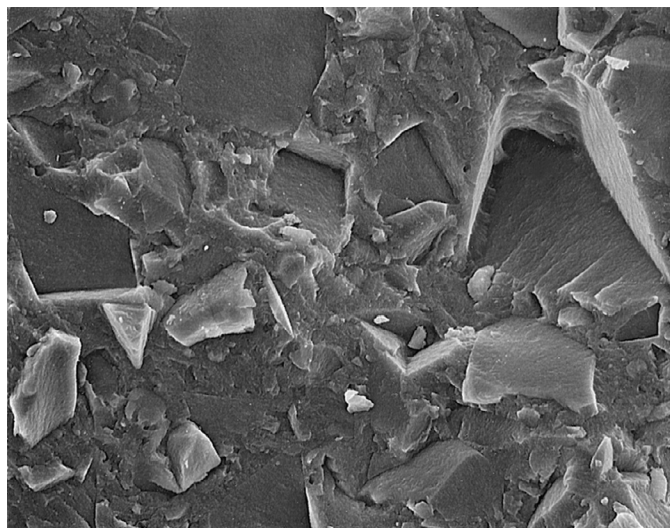
CRITICAL QUESTIONS

What features of microfilled resins make them the material of choice for certain types of restorations?
Which types of restorations are produced ideally from microfilled composites?

In the longer term, if microfilled composites are placed in wear-prone areas, they eventually break down and wear at a rate too fast for acceptable clinical performance. If placed in areas of proximal contact, anterior tooth “drifting” may occur. The wear process has also been related to fracture propagation around the poorly bonded “organic” filler particles (Figure 5-12). Thus diamond burs, rather than fluted tungsten-carbide burs, are recommended for trimming microfilled composites so as to minimize the risk of chipping. Microfilled composites are the resins of choice for restoring teeth with carious lesions in smooth surfaces (classes III and V) but not in stress-bearing situations (classes II and IV).

Nanofill Composites/Nanocomposites

More recently, nanoparticles (1 to 100 nm) have been fabricated by a different method from the pyrolytic precipitation process used for colloidal silica. This allows the individual, primary particles to be surface-coated (with γ -methacryloxypropyltrimethoxysilane, for example) *prior* to becoming incorporated into 3-D macromolecule chains, thereby preventing or limiting particle agglomeration into large networks and driving up viscosity. In essence, the particle size is similar to that in homogeneous microfill composites, but the difference is that the particles in homogeneous microfill composites are in three-dimensional agglomerates or networks that increase



• **Figure 5-12** Fractured microfilled composite. The fractured surface shows that the organic filler (composite filler) particles have been plucked out of the matrix resin, suggesting adhesive failure resulting from a weak interface between the precured microfill particles and the resin matrix. (Courtesy Dr. Karl-Johan Söderholm.)

viscosity, whereas those in nanofill composites are mostly discrete and have a minimal effect on viscosity. Thus these composites have optical properties and superior polishability like those of homogeneous microfill composites, but the surface treatment lowers the increase in viscosity when incorporated into the monomer, which

allows an increased filler loading of upward of 60% by volume and 78% by weight. Filler loading in this range is expected to lead to the necessary mechanical properties for use in posterior, stress-bearing restorations, but these properties have not yet been confirmed.

One of the reasons that increased mechanical properties are not observed is that no commercial products have as yet been reported to contain only isolated, discrete, homogeneously dispersed nanoparticles as the sole filler component. In fact, few if any dental resins currently designated as nanocomposites meet the strict requirement of having essentially all filler particles of less than 100 nm. This is because some of the nanoparticles exist as loosely bound “clusters” (loose agglomerates, such as in Filtek Supreme, 3M ESPE) of primary nanoparticles, which are sometimes reported to extend into the micron size range (e.g., 60 nm to 1.4 μm). Above 100 nm, clusters, like any particles, begin to scatter visible light and thereby reduce the translucency and the depth of cure of the composite. In addition, these clusters are not chemically bound to each other and act to decrease mechanical properties. Thus, although these nanocomposites with clusters have increased filler loading and hence better mechanical properties than a true homogeneous nanocomposite, they are not as strong as a hybrid composite.

To combat this deficiency, larger particles of either finely ground glass or prepolymerized nanoparticle-filled resin organic filler particles (essentially the same as those found in the micro-filled composites) are combined with the monomer-dispersed nanoparticles. Thus most, if not all, of these products are more accurately designated as “hybrid” nanocomposites or nanohybrids, consisting of a blend of two or more size ranges of filler particles, one or more of which is in the nanoparticle range (Table 5-1).

CRITICAL QUESTION

What are the relationships and tradeoffs among particle size, composition, and percentage of filler relative to their effect on the manipulation consistency, polishability, radiopacity, durability, and appearance of resin-based composite materials?

Hybrid (Large-Particle, Midfiller, Minifiller, Nanohybrid) Composites

As the name implies, hybrid composites are formulated with mixed filler systems containing large-particle, midfiller, minifiller, micro-fine, and/or nanofiller particles in an effort to obtain even better surface smoothness than that provided by the small-particle composites, while still maintaining the desirable mechanical properties of the small-particle composites. Thus they are a general utility class of composite that are also suitable for restoring certain high-stress sites where esthetic considerations dominate—for example, incisal edges and small noncontact occlusal cavities. They are widely used for anterior restorations, including class IV sites (Figure 5-13). Most commercial hybrid composites are marketed as nanohybrids because they are supposed to contain discrete nanofillers, but whether that is true or not, any hybrid could be marketed as a nanohybrid because hybrids contain nanoparticles. Thus checking whether the nanoparticles are discrete in aggregates or in clusters is important.

Most modern hybrid fillers consist of colloidal silica and ground particles of glasses containing heavy metals constituting a filler content of approximately 75% to 80% by weight. The glasses have an average particle size of about 0.4 to 1.0 μm , with a trend to steadily reduce this size range as improvements are made. In a typical size distribution, 75% of the ground particles are smaller than 1.0 μm , and colloidal silica represents 10% to



• **Figure 5-13** A class IV restoration made with a hybrid composite. **A**, Fractured maxillary central incisor prior to restoration. **B**, After restoration with a hybrid composite. (Courtesy Dr. William Rose.)

20% by weight of the total filler content. The smaller microfiller sizes increase the surface area, which generally increases the viscosity and requires a decrease in overall filler loading compared with small-particle composites. A polished surface is shown in Figure 5-14.

Classification of Composites by Manipulation Characteristics

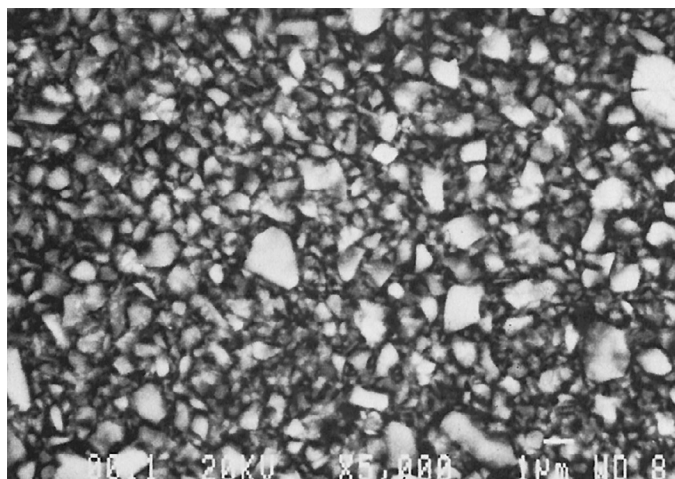
There are three distinct classes of composite materials based on the flow characteristics of the composite materials during the placement: flowable, condensable, and bulk fill.

CRITICAL QUESTION

What are the key modifications in formulation to make composites flowable?

Flowable/Injectable Composites

A modification of available composites resulted in the so-called *flowable* or *injectable* composites, which have become popular since 1995. These resins typically have a lower viscosity through a reduced filler loading, which enables the resin to flow readily, spread uniformly, intimately adapt to a cavity form, and produce the desired dental anatomy. This improves the clinician's ability to form a well-adapted cavity base or liner, especially in class II



• **Figure 5-14** Polished surface of a hybrid composite similar to those shown in Figures 5-12 and 5-14. Particle sizes range from about 0.1 to 3 μm (scanning electron microscope [SEM] magnification $\times 5000$). (Courtesy Dr. Robert L. Erickson.)

posterior preparations and other situations in which access is difficult. However, they are inherently inferior in mechanical properties because of the lower filler loading and higher susceptibility to wear and other forms of attrition. Because of their greater ease of adaptation and flexibility as a cured material, flowable composites are also useful in class V restorations in gingival areas and as the first base layer below a filling. They may also be applied in a manner similar to the use of fissure sealants as minimal class I restorations to prevent caries. Because they can flow into small crevice defects along restoration margins, some dentists refer to flowable resins as “dental caulk.”

CRITICAL QUESTION

What are the key modifications in formulation to make composites packable?

Condensable/Packable Composites

Compared with amalgam, the technique of composite placement is far more time-consuming and demanding. Because of their highly plastic, paste-like consistency in the precured state, composites cannot be packed vertically into a cavity in such a way that the material flows laterally and vertically to ensure intimate contact with the cavity walls. In particular, in the restoration of a tooth in which proximal contact with the adjacent tooth is required, the paste consistency of most composites dictates that a matrix band be carefully contoured and wedged to obtain acceptable proximal contact. These are tedious, time-consuming procedures and can produce variable results without a high level of skill. Thus *condensable composites* (also known as *packable composites*) were developed by adjusting their filler distribution to increase the filler loading and, hence, the strength and stiffness of the uncured material, and provide consistency and handling characteristics similar to those of lathe-cut amalgam. Note that the term *condensable* is misleading because unlike amalgam, where the material is condensed to “squeeze” out mercury to pack the amalgam alloy particles better and produce stronger restoration, the filler particles in composites are not packed more, and the resin is not “squeezed” out. Thus *packable* is a more accurate term for this type of composite.

In addition, the packable characteristics are derived from the inclusion of elongated, fibrous filler particles of about 100 μm in

length and/or rough-textured surfaces or branched geometries that tend to interlock and resist flow. This causes the uncured resin to be firm and resistant to slumping yet moldable under the force of condensers (“pluggers”). In certain products, larger-than-average filler particles (15 to 80 μm) are used, and the resin matrix is modified chemically to allow a slight increase in filler content over hybrids. Some have the same filler particles as their companion hybrids from the same manufacturer; the only difference is that the resin matrix is adjusted to allow approximately 1% to 2% of additional filler loading. However, many of the limitations of resin composites still prevail, and approximately twice the time required for amalgam placement is needed. At present, these materials have not demonstrated any advantageous properties or characteristics over the hybrid composites other than being somewhat similar to amalgam in their placement technique. Despite manufacturers’ claims to the contrary, conventional packable composites have not yet proven to be an answer to the general need for wear-resistant, easily placed posterior resins with low curing shrinkage and a depth of cure greater than 2 mm. A clinical study by van Dijken and Sunnegårdh-Grönberg reported that 6-year survival rates of two packable composites, Nulite F (Nulite Systems International) and Alert (Pentron), were 75% and 87%, respectively, and that the incorporation of fibers create very rough surface characteristics.

CRITICAL QUESTION

What are the key modifications in formulation to make composites bulk-curable?

Bulk-Fill Composites

Two main disadvantages of light-cured composites are the need of placing in 2-mm increments and the marginal gap formation resulting from polymerization shrinkage stress. Although 2-mm buildup reduces polymerization shrinkage stresses, this is very time-consuming for the clinician.

To address these shortcomings, bulk-fill composites that have a minimum of 4-mm depth of cure were introduced. This advancement has been made possible via the use of a combination of low-shrinkage monomers and greater translucency of the composite by better matching of refractive indices between the filler and resin. Other advancements include additional photoinitiators to enhance light curing (Ivoclar Vivadent EvoCeram Bulk Fill with Ivoceran) and/or the use of dual-cured initiator systems that allow for unlimited depth of cure (Parkell HyperFil, Apex Injectafil DC, and Coltene Fill-Up!).

Bulk-fill composites typically have good mechanical properties within the range of universal composites (transverse strength ~120 to 160 MPa and elastic modulus ~10 GPa), with very low shrinkage (<2% volumetrically). One study reported that despite being placed in a 4-mm layer, SDR Flow (Dentsply) performed just as well clinically as a nanohybrid placed in 2-mm layers after 5 years.

Because of the use of an amine-based activator, dual-cured bulk-fill composites are expected to have poorer initial color and color stability. Also, some studies have shown that only a few bulk-fill composites had volumetric shrinkages <2%, and that shrinkages may be more in the range between 1.7% and 3.5%. Finally, volumetric shrinkages are not well correlated to the production of shrinkage stress because shrinkage stress is not a material property, and various factors, such as rate of polymerization and composite modulus, affect shrinkage stress. In fact, the method of shrinkage-stress measurement strongly affects the measured stress values and sometimes, even sample ranking. Thus, although shrinkage stress

may be more important than volumetric shrinkage in predicting composite longevity, using this parameter to compare products is more difficult, and relative rankings would need to be used instead.

Bulk-fill composites may be too translucent to be esthetic. To address this concern, monomers that change in refractive index as they polymerize have been used so that this will match with the filler's refractive index before curing to allow deep light penetration. However, as the cure progresses, the composite will become opaquer and achieve a better match with the surrounding tooth structure. Examples include 3M Filtek One Bulk Fill Smart Contrast Ratio Management system and Ivoclar Tetric EvoCeram Bulk Fill Aessencio Technology.

The most recent advancement in bulk-fill composites is the introduction of bulk-fill flowable composites. Most of these products are recommended as the first layer of a restoration like conventional flowable composites, except this time, the first layer could be 4 mm (e.g., 3M Bulk Fill Flowable and Ivoclar Vivadent EvoFlow Bulk Fill). Thus only a second top esthetic layer is needed to complete the restoration, and often the corresponding bulk-fill composites from the same company are recommended with these bulk-fill flowables. The methods in making these bulk-curable are similar to those in regular bulk-fill composites, except the filler loading tends to be significantly lower to decrease viscosity (64 to 73 wt% vs. 77 to 87 wt% in conventional bulk-fill composites), and thixotropic properties are used to make these composites injectable. Despite that, transverse strengths are still in the range of regular bulk-fill composites (120 to 173 MPa), but the elastic modulus is lower, with some products having a deliberately lower modulus to reduce polymerization shrinkage stress (1.1 to 2.1 MPa) despite having higher volumetric shrinkage (2.5% to 3.5%). Examples include 3M Bulk Fill Flowable and Shofu Beautifil Bulk Flowable. A lower elastic modulus means the material is not as stiff, and hence, some polymerization stress is relieved.

CRITICAL QUESTIONS

What is the strategy of formulation that allows universal composites to be used in class I through V restorations?

Classification of Composites by Clinical Use

Filler particle size has predominantly determined the clinical use of the composite. In general, composites with smaller particles were used as anterior restorations because of their increased aesthetics but not in posterior applications because of their weaker mechanical properties, and the opposite was true for composites with larger particle sizes with higher filler loadings. However, the advent of hybrid composites makes formulations of universal composite applicable in all five classes of restorations. There are now universal, universal flowable, and universal bulk-fill composites. There is currently not enough information to meaningfully discuss universal bulk-fill composites except that an example is the GC America G-aenial BULK Injectable, so this topic is not included in this chapter.

The vast majority of new universal composites are nanohybrids with good combinations of high filler loading, mechanical properties, and esthetics. Exceptions include the 3M Filtek Supreme Ultra and Kerr Premise, which are nanofills. However, Filtek Supreme Ultra contains nanoclusters that are in the micron-size range, and Premise contains prepolymerized fillers (PPFs) similar to nanohybrids. Universal composites are typically highly filled (75% to 89% fill by weight and up to 70% by volume) to impart

very good mechanical properties with transverse strengths between 100 and 170 MPa and a modulus between 7 and 11 GPa. The nanoparticles help enhance esthetics to allow for anterior placement. In addition, many products (e.g., Kerr Premise, Dentsply Sirona TPH Spectra ST, GC America Kalore, and Ivoclar Tetric EvoCeram) contain larger PPFs that not only allow for increased filler loading but also allow for greater polishability because the PPFs are polymer based. Several products have also modified fillers and their refractive indices to produce a chameleon effect (e.g., GC America Gradia Direct X and Kalore, and Kerr Harmonize and Herculite Ultra) to enhance the ease of color matching.

The universal flowable category is misleading because many are for cavity base linings for the corresponding universal composite or only for class V restorations. As such, they are not universal composites. Those truly universal flowable composites have flexural strengths, moduli, wear, and esthetic properties in the range of universal composites, and their flowability is produced through the system's thixotropic properties, which allow these composites to flow under pressure and be injected but become more elastic and prevent slumping. Hence, some products may be called "injectable" rather than "flowable." Their flow properties are in the low-flow range of flowable composites. Again, most of these products are nanohybrids, except GC America's G-Aenial Universal Flo and G-Aenial Universal Injectable, which are nanofills with modified silanation to increase filler loading (69% by weight and 50% by volume) and the bond between the resin and filler to increase mechanical properties. Other examples of universal flowable composites include Shofu Beautifil Flow Plus X and VOCO GrandioSo Flow and Heavy Flow.

Classification of Composites by Unique Properties

As composites have become the dominant materials in restorative dentistry, they have also been formulated to address additional demands from the material. The unique properties discussed in this section include low-shrinkage composites, self-adhesive flowable composites, and bioactive composites.

Low-Shrinkage Composites

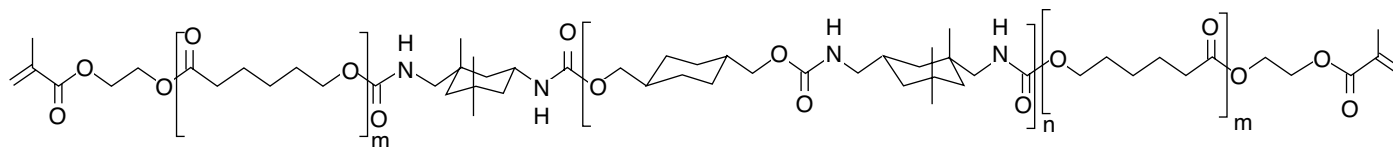
With polymerization shrinkage being a major deficiency with dental composites, there have been many advancements to develop low-shrinkage composites. These advancements can be separated into advancements that maximize filler loading and those in low-shrinkage monomers.

Maximizing Filler Loading

The role of fillers in reducing polymerization shrinkage has been discussed earlier. The first dental composite marketed as a low-shrinkage composite was the Bisco Aelite LS with optimized filler loading as high as 89% by weight and 75% by volume, which is still the highest filler loading by volume reported. The Aelite LS has a filler particle size range of 0.04 to 3.5 μm and a volumetric shrinkage of 1.5%, but because of the larger particles, this material is only recommended for posterior class I, II, and VI restorations and not for aesthetic applications.

CRITICAL QUESTION

What are the key strategies used in the new monomers to make composites low shrinkage?



• **Figure 5-15** A high-molecular-weight polyurethane dimethacrylate monomer, DX-511, that contains a long, rigid central section between flexible methacrylate end groups (Kalore, GC America, Alsip, IL). Like urethane dimethacrylate (UDMA), DX-511 has urethane ($-\text{NH}-\text{CO}-\text{O}-$) groups that connect a central segment between two ethylmethacrylate end groups. It also contains $2m + 1$ cyclohexane rings. (Courtesy Dr. Barry K. Norling.)

The Shofu Beautifil Bulk Restorative similarly has a filler loading as high as 87% by weight and 75% by volume and a volumetric shrinkage of 1.7%. This material is also only indicated for posterior, nonaesthetic class I and II applications. Interestingly, the Shofu Beautifil II LS has lower filler loading at 83% by weight but lower volumetric shrinkage at 0.85%, yet higher shrinkage stress than the Beautifil Bulk Restorative (2.72 MPa vs. 1.06 MPa, respectively). This surprising difference in shrinkage stress is caused by Beautifil Bulk Restorative having a lower elastic modulus.

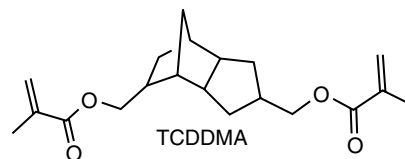
Low-Shrinkage Monomers

The influence of monomers on polymerization shrinkage has also been discussed earlier. In this section, we will discuss four monomers that have been used to formulate low-shrinkage composites.

Kalore, also known as *DX-511* (GC America) (Figure 5-15), has a high molecular weight and a long rigid central section with flexible methacrylate end groups; these provide rodlike shapes that facilitate self-assembly into compact molecular structures. This, together with dilution of the number of polymerizable end groups as a result of the high molecular weight (895 vs. 512 for *bis*-GMA), reduces polymerization shrinkage, and the flexible end groups promote reactivity and enhance monomer–polymer conversion.

N'Durance (Septodont USA) is a dimer dicarbamate dimethacrylate (DDCDMA) product that also contains a bulky central group, somewhat analogous to TDC-urethane dimethacrylate. The bulky center is made up of a six-carbon aliphatic ring with two long hydrocarbon side chains derived from a linoleic acid dimer (Figure 5-16). The center section is connected to two methacrylate end groups via urethane groups ($-\text{NH}-\text{CO}-\text{O}-$, also referred to as *carbamate* groups). The chain length between reactive ends is very long (having a molecular weight of 843), similar to that of DX-511 (see Figure 5-15), which provides double-bond dilution and hence reduced shrinkage; the bulky center section allows greater conversion during copolymerization and greater stress relaxation prior to the gel point. A further advantage is the hydrophobic nature of the center group, which restricts water absorption and solubility with the other dimethacrylates in the formulation. This leads to the formation of two separate phases during polymerization and produces a small expansion that partially offsets the polymerization shrinkage.

Venus Diamond (Kulzer) is a resin product based on 4,8-di(methacryloxy methylene)-tricyclodecane (TCDDMA), a bulky, space-filling dimethacrylate monomer (Figure 5-17). The bulky three-ring central group provides steric hindrance, which holds the monomers apart and thus slows the rate of polymerization. This lengthens the time needed for the crosslinking reaction to reach the gel point and provides time for adjacent



• **Figure 5-16** 4,8-Di(methacryloxymethylene)-tricyclodecane (TCDDMA), a bulky, space-filling urethane dimethacrylate monomer.

polymer chain segments to slip among themselves, rearrange to lower-energy configurations, and relieve developing stresses before the gel point is reached, resulting in one of the lower-curing-stress resins currently reported among commercial products.

Filtek LS (3M ESPE) involves an entirely different chemistry based on epoxy, rather than acrylic functionality. This product is no longer available on the market but is included here in case future products contain epoxy chemistry. These tetra-functional “silorane” monomers (Figure 5-18) use ring-opening polymerization. Silorane chemistry uses a combination of epoxy functionality (three-unit ring with two carbons and one oxygen) combined with siloxane units ($-\text{O}-\text{Si}-\text{O}-$) that can be cured with low shrinkage via a cationic crosslinking mechanism by means of ring-opening polymerization. When the rings open, they lengthen and occupy more space; the resulting expansion offsets a substantial proportion of the polymerization shrinkage. Previously, epoxy systems were not used for dental applications because a nontoxic curing initiator with hydrolytic stability could not be found.

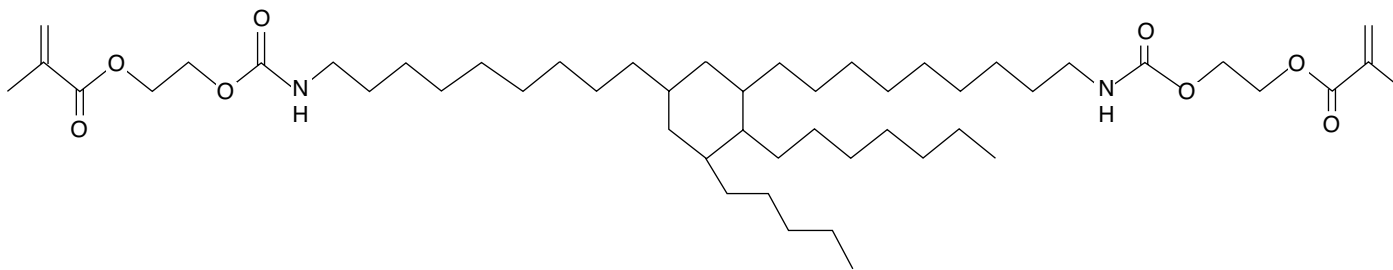
CRITICAL QUESTION

What technology is employed to make composites self-adhesive?

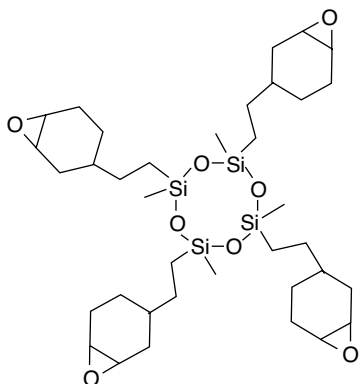
Self-Adhesive Flowable Composites

The process of bonding composites to the tooth is complicated. As such, the development of dentin bonding agents has gone from “three step” to “one step” with one bottle of liquid. Self-adhesive flowable composites, which contain self-etching and adhesive monomers for bonding to hydroxyapatite, may practically eliminate the bottles and the use of a separate bonding agent. These composites would be used like conventional flowable composites in small class I cavities, as a first or base layer under fillings, and as pit and fissure sealants, but without the need for a bonding agent.

Currently, three commercial self-adhesive flowable composites exist, each containing a monomer that etches and adheres to tooth structure. DMG Constick contains 10-methacryloyloxydecyl dihydrogen phosphate (MDP) monomer, which was found to form stable bonds with hydroxyapatite with the formation of 10-MDP-Ca salts. Kerr Vertise Flow contains glycerol phosphate dimethacrylate (GPDM) monomers, which have



• **Figure 5-17** Dimer dicarbamate dimethacrylate (DDCDMA), a phase-separating cycloaliphatic urethane dimethacrylate with a bulky center, is composed of a six-carbon aliphatic ring with two long hydrocarbon side chains derived from a linoleic acid dimer. (Courtesy Dr. Barry K. Norling.)



• **Figure 5-18** Tetrafunctional silorane monomer polymerizes via a cationic-initiated, epoxy-ring-opening, crosslinking mechanism. When the rings open, the chains lengthen and occupy more space and partially offset the polymerization shrinkage. (Adapted from Weinmann W, et al: Siloranes in dental composites. *Dent Mater* 21:68–74, 2005.)

a strong etching effect but form a weaker chemical bond with hydroxyapatite compared with other self-adhesive monomers. Pentron Fusio Liquid Dentin uses 4-methacryloxyethyl trimet-ellitic acid (4-META) to etch and bond via its carboxylate groups to the calcium in hydroxyapatite.

Product brochures show dentin shear bond strengths of 24, 20, and 15 MPa for Constic, Vertise Flow, and Fusio Liquid Dentin, respectively. However, Peterson et al. reported that after thermocycling for 5000 cycles at temperatures of 5 to 55 °C, dentin bond strengths deteriorated to 0.3, 0.7, and 2.4 MPa, and enamel bond strengths deteriorated to 3.9, 1.4, and 2.5 MPa for Constic, Vertise Flow, and Fusio Liquid Dentin, respectively. The results are suspected to be caused by the low filler loading of these flowables and the hydrophilic nature of the self-etching and adhesive monomers, which may increase water imbibition and subsequent polymer degradation.

CRITICAL QUESTIONS

What is the main characteristic of a bioactive composite?
Which released ions are responsible for hydroxyapatite formation?

Bioactive Composites

The definition of a *bioactive material* in biomedical science is a material that is not just biocompatible or bioinert but one that produces a favorable biological response, such as repair or regeneration of tissue. In dental materials, bioactive materials have

traditionally included those that release fluoride ions, such as glass ionomers, resin-modified glass ionomers (RMGIs), and compomers (Chapter 7, *Glass Ionomer Cement and Combination Cements*). Released F^- ions can induce remineralization and bind with apatite to form stronger fluorapatite to protect the tooth from acid demineralization. However, glass ionomers and RMGIs are not very aesthetic and have poor mechanical properties. As such, they are mainly used as class V restorations and as cements.

New and improved bioactive composites include DMG's Ecosite Bulk Fill composite, Parkell's Predicta Bioactive composites (Bulk, Core-Stackable, and Core-Flowable), Shofu's Beautifil composites (II LS, Bulk Flowable, Flow Plus, and Flow Plus X), and Pulpdent's ACTIVA BioACTIVE restorative. Interestingly, DMG's Ecosite Bulk Fill composite is not marketed as a bioactive composite, despite claims that this product releases F^- ions. Parkell's Predicta Bioactive composites simply release Ca^{2+} , PO_4^{3-} , and F^- to trigger apatite formation. However, there is currently not much information available for how Predicta Bioactive composites release these ions.

Shofu's Beautifil composites are "hybrid" composites called *Giomer* that are like RMGIs and compomers with modified filler. The aim is to combine the fluoride-releasing and recharging ability of glass ionomers with the mechanical properties of nanohybrid composites. The advancement here is that instead of using alumino-silicate glass particles to release F^- ions, Gionomers use fluoro-boro-alumino-silicate glass particles with a surface coating of a glass ionomer trapped in a polyacid matrix to also release Na^+ , Sr^{2+} , Al^{3+} , SiO_4^{4-} , and BO_3^{3-} . The SiO_4^{4-} and F^- ions are used to promote remineralization, and the F^- and Sr^{2+} ions are used for converting hydroxyapatite to the stronger fluoro-apatite and strontium-apatite. The ion exchange from Giomer fillers is also supposed to neutralize acid that leads to tooth demineralization.

Pulpdent's ACTIVA BioACTIVE restorative is a dual-cured RMGI/compomer, which is based on urethane dimethacrylate that increases composite toughness and reduces wear compared with RMGIs and compomers. This composite releases and recharges with Ca^{2+} , PO_4^{3-} , and F^- to stimulate apatite formation and teeth remineralization and releases more PO_4^{3-} under acidic conditions to claim its "smart" material status. This product is also self-adhesive as a result of the polyacrylic acid in the glass ionomer component and phosphate-based monomers in the ionic resin (Chapter 7, *Zinc Polycarboxylate Cement and Glass Ionomer Cement*). The system is a dual-cured material that uses an automix syringe that will entail some of the disadvantages inherent in dual-cured composites. Its transverse strength is toward the lower end of universal composites (120 MPa). However, a 2019 randomized controlled study by van Dijken et al. suggested that ACTIVA

BioACTIVE, as used in posterior restorations, may not bond to dentin or prevent secondary caries. The article cited a significantly higher failure rate compared with a nonbioactive nanofill composite as soon as 1 year (24.1% vs. 2.5%, respectively) as a result of lost restorations, postoperative symptoms, and secondary caries.

Properties of Resin-Based Composites

Table 5-3 presents a compilation of selected physical and mechanical properties of various types of composites. Additional properties described in this section include degree of cure, resin matrix constrain, strengthening mechanism, curing shrinkage and shrinkage stress, wear, clinical longevity, placement time, and biocompatibility.

Degree of Conversion

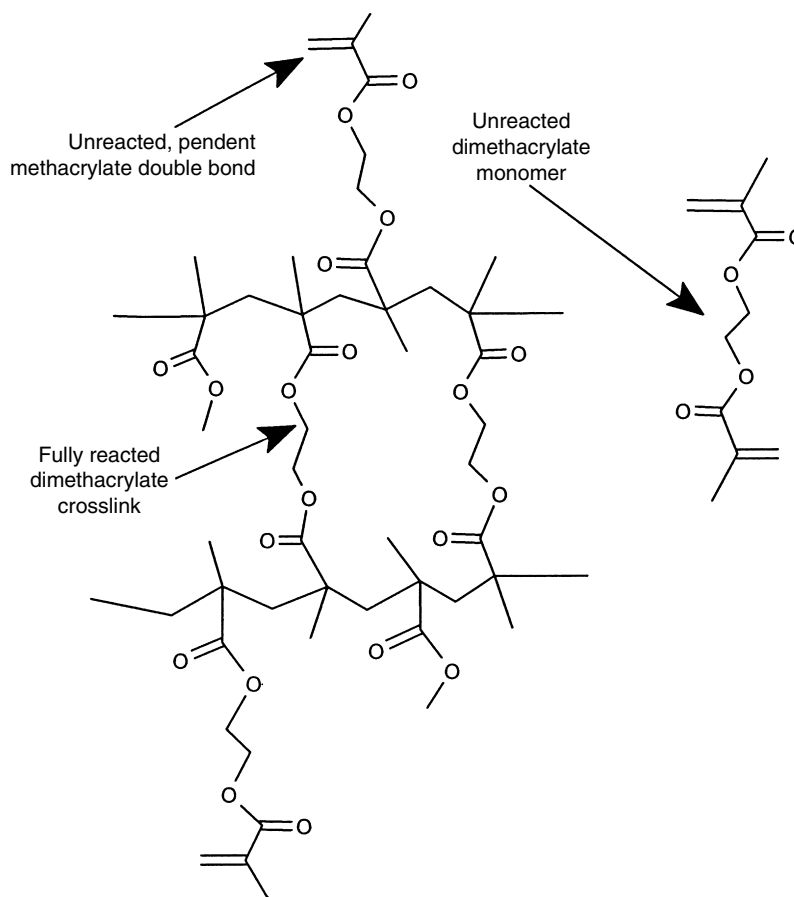
The DC is a measure of the percentage of carbon–carbon double bonds that have been converted to become part of a polymeric chain (Figure 5-19). The higher the DC, the better the strength, wear resistance, and many other properties essential to resin performance. A conversion of 50% to 60%, typical of highly cross-linked *bis*-GMA–based composites, implies that 50% to 60% of

the methacrylate groups have polymerized. This does not mean that 40% to 50% of the monomers are left unpolymerized in the resin. The most likely scenario is that one of the two methacrylate groups per dimethacrylate molecule is covalently bonded to the polymer, with the rest of the molecule forming a pendant group.

Conversion of the monomer to a polymer depends on the resin composition; the irradiance of the light source; the light transmission through the material; and the concentrations of sensitizer, initiator, and inhibitor. The total DC within resins does not differ between chemical-activated and light-activated composites containing the same monomer formulations as long as adequate light curing is employed. Conversion values of 50% to 70% are achieved at room temperature for both curing modes. Likewise, the polymerization shrinkage of comparable light-activated and chemical-activated resins is not significantly different.

Matrix Constraint

When thermal expansion arises, the interfacial bond between the resin matrix and the filler with a lower coefficient of thermal expansion (nearly zero in some cases) prevents the resin matrix from pulling away and, thus, reduces expansion of the matrix.



• **Figure 5-19** The degree of conversion reflects the percentage of methacrylate double bonds that are converted to single bonds during the curing reaction. This figure shows that a cured resin can contain dimethacrylate groups with zero, one, or two unreacted double bonds. If at least one double bond has reacted, the dimethacrylate group is bound to the polymer network as a “pendant” group with one double bond available for further reaction. Any completely unreacted monomers can migrate out of the cured resin. Crosslinked groups strengthen and make the resin rigid, whereas pendant groups plasticize the resin, and unreacted monomer softens and swells the resin structure, as explained in [Chapter 2, Thermal Properties](#).

Conversely, during cooling, the matrix contracts and decreases the space occupied by the filler, but because the filler occupies that space, full contraction is prevented or reduced.

This constraint does have limits. During expansion, the composite can fracture within the matrix because of the added tension at the resin–filler interface, depending on whether the interfacial bond is stronger than the fracture toughness of the filler or the matrix. In contraction, the composite can fracture within the matrix or within the filler particle, depending on which is weaker.

Strengthening Mechanism

The strength of composites is highly dependent on the bonding between the weak matrix and the strong filler particles. Without the coupling agent, the filler particles cannot absorb stresses in the matrix and act as if they were voids. Thus a crack traveling through the matrix simply bypasses the particles. The energy required to detour around noncoupled particles is lower because the lack of coupling at the filler–matrix interface makes this interface behave as an existing “crack.” In a true composite, as the crack propagates to a bonded filler particle, the crack must pass around the particle because the filler particle is stronger than the matrix and the interfacial bond. Thus the path the crack must take around the particles has to be created, and the creation of the new path requires additional energy. The additional energy needed must come from the increase of the external stress acting on the composite. This makes the composite tougher.

If the interfacial bond is weaker than the matrix, a process of crack blunting occurs (Figure 5-20). As the crack propagates to the weak interface, a void or tear opens up in front of the advancing crack because of the stresses that the weak bond experiences. However, this void is perpendicular to the propagating crack; thus when the crack arrives, the tip of the crack has been blunted, and more stress is required to propagate the crack.

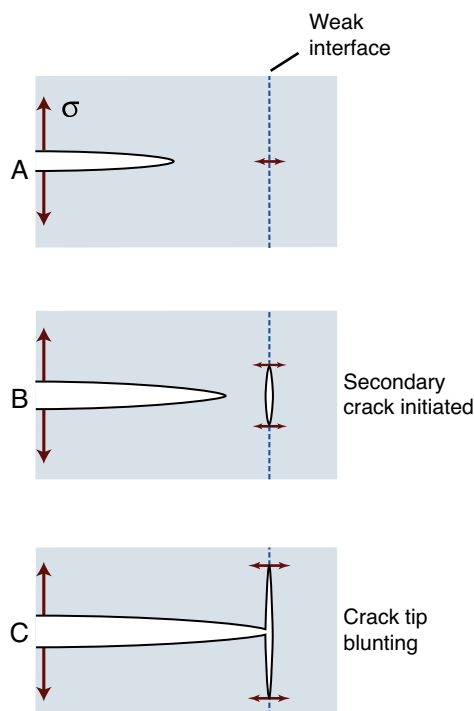
Note that the use of a crosslinked polymer matrix also increases toughness because the crosslinkage prevents the polymer chains from being drawn and separated as the crack propagates. However, the material then becomes brittle.

CRITICAL QUESTIONS

What are the problems that result from shrinkage and curing-induced marginal stress during the polymerization of restorative resins? How are polymerization stresses affected by the presence of reinforcing fillers in dental composites?

Cure Shrinkage and Managing Shrinkage Stress

Cure shrinkage arises as the monomer is converted to polymer because the free space a polymer chain occupies is about 20% less than that of a matching number of monomers. During the early stage of the polymerization, the material is still soft, and that allows the growing polymer chains to adjust their position to relieve the stress they are under. When polymerization reaches the **gelation** or the **gel point**, and the material begins to become rigid, the growing chains will not be able to move as easily and thus become stressed as polymerization progresses. The resultant polymerization stress can be affected by the total volume of the composite material, the type of composite, the polymerization rate, and the ratio of bonded/nonbonded **surfaces** or the configuration of the tooth preparation (**C-factor**). These stresses tend to develop at the tissue–composite interface, stressing the bond, and eventually producing a gap at the



• **Figure 5-20** Crack propagation near weakly bonded interface. **A**, A crack propagates toward a weak interface under the influence of a tensile stress. **B**, A secondary crack initiated at the weak interface when the stress induced at the interface is greater than the interfacial bond strength. **C**, When the main crack reaches the secondary crack, its propagation is impeded by a process called *crack blunting*. (Adapted from Darvell BW: *Materials Science for Dentistry*, ed 10, Cambridge, UK, 2018, Woodhead Publishing Ltd.)

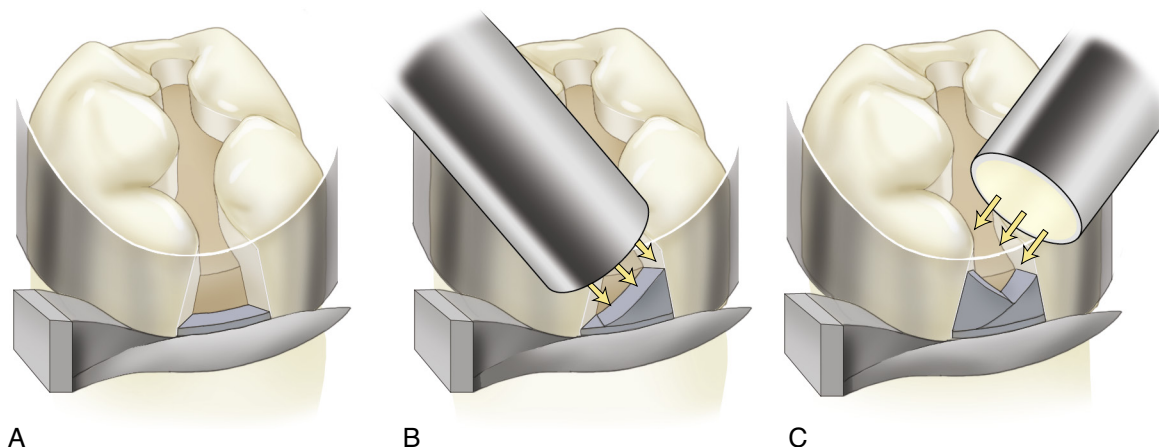
restoration margins. Consequently, the risk for marginal leakage and the ensuing problems of marginal staining and secondary caries are exacerbated. Undoubtedly, this is one of the greatest problems of composites used for class II and V restorations.

As discussed previously, light-activated resins give the operator control of working time and eliminate porosity from mixing the two-part systems of chemical-activated resins. However, the internal pores in self-cured resins act to relax residual stresses that build up during curing (the pores enlarge during hardening and reduce the concentration of stresses at the margins). Also, the slower curing rate of chemical activation allows a larger portion of the shrinkage stress to relax by internal flow before the gel point.

Two general approaches have been followed in seeking to overcome the problem of stress concentration and marginal failure experienced with light-activated resins: reduction in volume contraction by altering the chemistry and composition of the resin system and clinical techniques designed to offset the stresses caused by polymerization shrinkage. Reduction in volume contraction has been achieved by using larger monomers to “dilute” the number of double bonds that need to be reacted and by the addition of fillers that reduce the quantity of resin needed in the composite. Some low-shrinkage monomers are described earlier in the Low-Shrinkage Composites section. Clinical techniques involving incremental buildup and control of the curing rate are described in the following sections.

CRITICAL QUESTION

How can the composite clinical manipulation technique be used to improve the integrity of the marginal seal in a composite restoration?



• **Figure 5-21** Incremental buildup of the box. **A**, First incremental layer of resin composite (gray area) has been placed and cured. **B**, Second increment being cured with a light source. **C**, Third composite increment during curing.

Incremental Buildup and Cavity Configuration

One technique attempts to reduce the C-factor, which is related to the geometry of the cavity preparation and represented by the ratio of bonded to nonbonded surface areas. Residual polymerization stress increases directly with this ratio. During curing, shrinkage leaves the bonded cavity surfaces in a state of stress; the nonbonded, free surfaces (i.e., those that reproduce the original external tooth anatomy) relax some of the stress by contracting inward toward the bulk of the material. A layering technique (Figure 5-21) in which the restoration is built up in increments, curing one layer at a time, effectively reduces polymerization stress by minimizing the C-factor. That is, thinner layers reduce the bonded surface area and maximize the nonbonded surface area, thus minimizing the associated C-factor. Thus an incremental technique overcomes both the limited depth of cure of most light-cured composites and the residual stress concentration but adds to the time and difficulty of placing a restoration.

Soft-Start, Ramped Curing, and Delayed Curing

Another approach that is used to offset light-activated polymerization stress buildup is to follow the example of chemically initiated systems by providing an initial low rate of polymerization, thereby extending the time available for stress relaxation before reaching the gel point. This can be accomplished by using a soft-start technique, whereby curing begins at low light irradiance and finishes with high irradiance. This approach allows for a slow initial rate of polymerization and a high initial level of stress relaxation during the early stages and ends at the maximum irradiance once the gel point has been reached. This drives the curing reaction to the highest possible conversion only after much of the stress has been relieved. A number of studies have demonstrated that varying levels of stress reduction in tooth-cavity walls can be achieved in this way, while not increasing the total exposure time or sacrificing either degree of cure or depth of cure. Consequently, a variety of protocols have been developed and the necessary lamps made available that automatically provide one or more soft-start exposure sequences.

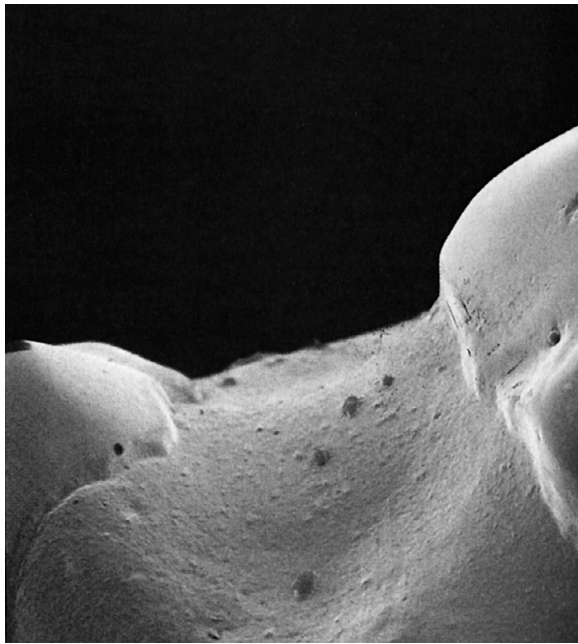
Variations of this technique include ramping and delayed cure. In ramping, the irradiance is gradually increased or “ramped up” during the exposure. Such ramping employs stepwise, linear, or exponential modes. In delayed curing, the restoration is initially

incompletely cured at low irradiance. The clinician then sculpts and contours the resin to the correct occlusion and later applies a second exposure of light for the final cure. This delay allows substantial stress relaxation to take place. The longer the time that is available for relaxation, the lower is the residual stress that is expressed. Delayed curing and exponential ramp curing appear to provide greater reductions in curing stress but do require more time.

In response to this situation, care should be taken when high-irradiance lamps are used. Increased lamp irradiance allows for shorter exposure times for a given depth of cure in a particular shade and type of resin. Thus these high-irradiance lamps should, in principle, provide substantial savings in chair time. However, a high-irradiance, short-exposure time causes an accelerated rate of curing, which inevitably leads to substantial residual stress buildup because of the inherently less time for stress-relaxation mechanisms to take place. Because of these tradeoffs, there appears to be little advantage to ramped, delayed, or soft-start curing techniques. Numerous laboratory studies and some clinical evidence support this conclusion. Thus the clinician should carefully consider the tradeoffs before investing in these more expensive types of curing lamps.

Wear

In addition to polymerization shrinkage, other frequent clinical problems have been occlusal (Figure 5-22) and interproximal wear, especially in the case of posterior composites. The mechanism of occlusal wear is a complex problem that has been the subject of much research. Unfortunately, before clinical use, abrasion and wear resistance can be measured only by a laboratory test that simulates simplified environmental conditions. As of yet, no single test method has been agreed upon as a valid predictor of clinical performance. Although several laboratory test methods are useful to guide research and development efforts, controlled clinical evaluations are the only reliable means of evaluating the durability and useful lifetime of restorative materials. However, based on such studies, the best composites designed for posterior restorations still wear more than natural enamel under identical conditions. Although wear-rate differences of 10 to 20 $\mu\text{m}/\text{year}$ may seem small for posterior composites, this wear rate still amounts to 0.1 to 0.2 mm more than enamel over 10 years. Thus being cautious is important in selecting the clinical cases to be treated with posterior composites.



• **Figure 5-22** Scanning electron micrograph of a 9-year-old small-particle-filled composite, illustrating generalized wear surface by three-body wear. (Courtesy Dr. Robert L. Erickson.)

Two principal mechanisms of composite wear have been proposed. The first mode is two-body wear, based on direct contact of the restoration with an opposing cusp or with adjacent proximal surfaces to mimic the high stresses developed in the small area of contact. This is related to the higher force levels exerted by the opposing cusp or forces transferred to proximal surfaces.

The second mode is three-body wear, which simulates the loss of material in noncontact areas, most probably owing to contact with food as this is forced across the occlusal surfaces. This type of wear is affected in a complex way by a number of composite properties, such as toughness, porosity, stability of the silane coupling agent, degree of monomer conversion, filler loading, and the sizes and types of filler particles.

Clinically, although direct tooth-to-restoration contact occurs infrequently during mastication, the loss of material caused by direct wear in areas of tooth-to-tooth contact appears to be greater than that of three-body abrasion by food in noncontact areas. Composites in which the filler particles are small (1 μm or less), high in concentration, and well bonded to the matrix are the most resistant to wear. Large restorations tend to wear more than smaller ones do, such as in restorations in molars compared with those in premolars.

Variations among patients—such as differences in chewing habits, force levels, and variations in oral environments—also play a significant role in the wear process. A typical wear pattern for a composite is shown in [Figure 5-22](#) for a 9-year-old, chemical-activated, small-particle-filled composite restoration. Although the loss of material shown in this figure is more severe than that for current restorative materials, the image illustrates the wear phenomenon. Notice the smoother anatomical contours and the exposed cavity walls where the composite has been worn away by abrasion.

The major indications for class II composite restorations place emphasis on the demand for esthetics. A conservative preparation is preferred so that the tooth, rather than the composite, absorbs

more of the stress. The dentist must also be familiar with the rigorous placement procedures essential for success, as described in textbooks on operative dentistry. However, there are obvious contraindications. A composite class II restoration is doomed to failure in the mouth of a patient who bruxes because of the greater potential for wear. The use of posterior composites in a caries-active mouth is also questionable because few current restorative materials have the ability to provide an anticariogenic effect or to resist leakage. If composites are used for such situations, the application of a hydrophilic sealing resin along the margins may be beneficial. Nonetheless, with the greater demand for esthetics and continual improvements in composite formulations, the use of these materials in stress-bearing situations continues to increase. In response, academic and industry research can be expected to continue to improve the clinical durability of composite materials (see later discussion of the longevity of composites).

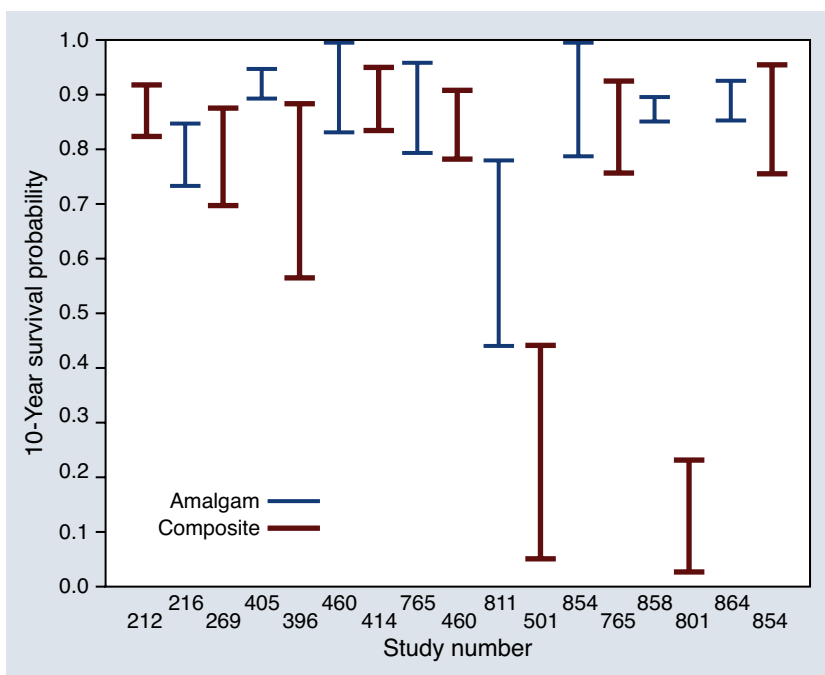
The problem of wear in posterior resin applications has been considerably reduced by ongoing advances in composite technology. Nevertheless, difficulties still exist in high-stress situations related to inherent problems with both the mechanical and chemical degradation of composites. However, polymerization shrinkage, technique sensitivity, and difficulty in obtaining a predictable and reliable bond to dentin or cementum margins are probably more important. These deficiencies remain a major concern regarding the potential leakage associated with class II restorations.

Longevity of Composites

The most commonly cited reasons for the failure of composites in clinical studies are secondary caries, fracture, marginal deficiencies, and wear. However, these reasons vary greatly depending on the type of study (randomized clinical trial versus private-practice setting), type of composite used, period of observation, and other aspects of study design. Nonetheless, when properly placed, composites can last for many years even in posterior regions, where wear and bite forces are greatest. The clinical performance of dental restorations is best judged on the basis of long-term clinical trials, preferably those based on randomized controlled designs. However, very few studies of this type exist in the dental literature. We are using four studies to discuss the longevity of composites.

A critical review of clinical data over 10 years by Chadwick et al. shows that the survival rates of composites are significantly lower than those of amalgam. Amalgam also demonstrated less variability in survival rates ([Figure 5-23](#)). The comparative survival rates for amalgam versus composite restorations in permanent teeth at 3, 4, 5, and 7 years are summarized in [Table 5-4](#). Similar comparative data for restorations in primary teeth after 3 and 4 years are also listed in this table. The overall survival rate for composites in permanent teeth after 7 years was 67.4%, compared with 94.5% for amalgam restorations. More than 90% of amalgam restorations in permanent teeth survived longer than 9 years. In comparison, only 64% of glass ionomer restorations survived after 5 years. Only 41% of class V composites placed with dentin bonding agents survived longer than 5 years. The study concluded that the class II glass ionomer/composite restorations should be avoided because of a high percentage of failures at the gingival margin of the proximal box.

In a retrospective study on the longevity of 1955 posterior composites placed between 1990 and 1997 in a private-practice setting,



• **Figure 5-23** Ten-year survival probability for posterior composite and amalgam restorations. (Data from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*, York, UK, 2001, National Health Service Centre for Reviews and Dissemination, University of York.)

TABLE 5-4 Comparison of Survival Probabilities for Various Types of Restorations after 3, 4, 5, and 7 Years

Restoration Type	3 Years		4 Years		5 Years		7 Years	
	Primary Teeth	Permanent Teeth	Primary Teeth	Permanent Teeth	Primary Teeth	Permanent Teeth	Primary Teeth	Permanent Teeth
Amalgam	95.3	97.2	95.1	96.6	90.8	95.4	—	94.5
Composite	82.4	90.0	67.2	85.6	—	78.2	—	67.4
Glass ionomer	51.5	73.8	51.5	73.8	31.2	64.9	—	—
Class V composite with DBA	—	83.7	—	47.7	—	41.5	—	—
Ceramic or composite inlay	—	93.3	—	90.1	—	85.3	—	—

DBA, dentin bonding agent.

Modified from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*, York, UK, 2001, National Health Service Centre for Reviews and Dissemination, University of York.

Opdam et al. reported a survival rate for composite resin of 91.7% at 5 years and 82.2% at 10 years. There was a significant effect of the size of restored surfaces on the survival of the restorations—that is, the more conservative the restoration, the longer these restorations survived.

In a 22-year follow-up of 362 restorations placed between 1986 and 1990, da Rosa Rodolpho et al. reported survival rates of midfill hybrid composites at 74% and minifill hybrid composites at 64%, respectively. The study also reported that the annual failure rate in the second part of the observation period had become constant for midfill composites, whereas minifill composites had shown an increase, suggesting that the physical properties of the composite might have some impact on restoration longevity.

One systematic review by Alvanforoush and colleagues compared composite failure between the two decades of 1995 to 2005 and 2006 to 2016 using studies that were at least 24 months long. Twelve studies that were used for the systematic review had observation periods of posterior composites of longer than 6 years. Five were published between 1995 and 2005 and observed posterior composites for 10 years. Seven were published between 2006 and 2016 that ranged from 6 to 22 years. Interestingly, overall, they found that composite survival rates actually decreased from 89.4% in the studies from 1995 to 2005 to 86.9% in the studies from 2006 to 2016. However, the incidence of failure from secondary caries decreased from 29.5% to 25.7%, and additionally, the incidence of composite fracture increased from 28.8% to

39.1%. The authors note that these findings may be attributable to the increased use of composites for larger restorations. Table 5-5 summarizes long-term survival rates for the different types of composites in this review.

Placement Time of Composites

Although the performance of posterior composites has greatly improved during the past decade relative to amalgams, the placement time is significantly longer for composites and much longer for ceramic and composite inlays (Figure 5-24). Obviously, the cost of restorations for the patient is also proportionately higher for the inlay prostheses. In fact, the relative cost per tooth per year over a 5-year period in terms of multiples for amalgam is 1, composite is 1.62, and ceramic or composite inlay restorations is 6.35. The relative cost per tooth per year of amalgam restorations is significantly less than that of composites after 10 years (1 vs. 3.36). A comparative analysis of the placement times is summarized in Table 5-6 for class I, class II (two-surface), class II (three-surface, mesial-occlusal-distal), and pin-retained cusp replacement restorations.

TABLE 5-5 Long-Term Survival Rates of Different Types of Composites

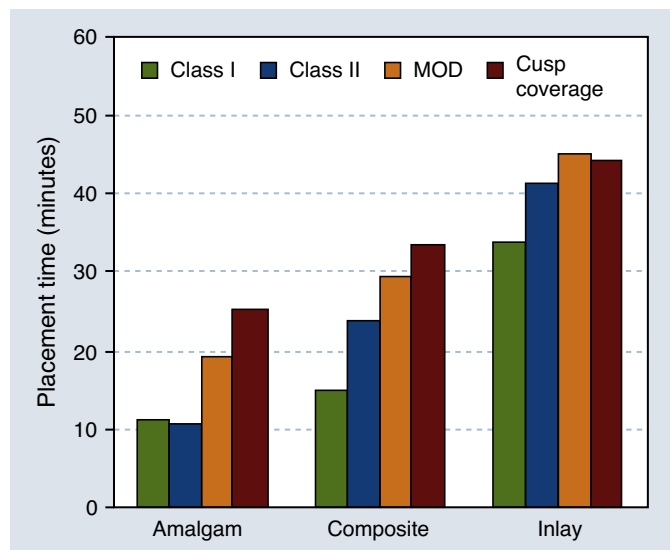
Composite Type	Study Term (Failure Mechanism)	Survival Rate
Fiber-reinforced packable	6 y	75%–87%
Midfill	22 y	74%
Minifill	22 y	64%
Hybrid	10 y	80%
	10 y (secondary caries)	40%
	15 y (wear)	74%
	18 y (fracture)	70%
Low shrinkage	15 y	77%
Universal nanohybrid	10 y	97%

Adapted from Alvanfroush N, et al: Comparison between published clinical success of direct resin composite restorations in vital posterior teeth in 1995–2005 and 2006–2016 periods. *Aust Dent J* 62(2):132–145, 2017.

Biocompatibility of Composites

A chemical insult to the pulp from composites is possible if components leach out or diffuse from the material and subsequently reach the pulp. Inadequately cured composite materials at the floor of a cavity can serve as a reservoir of diffusible components that can induce long-term pulp inflammation. This situation is of particular concern for light-activated materials. If a clinician attempts to polymerize too thick a layer of resin or if the exposure time to the light is inadequate (as discussed previously), the uncured or poorly cured material can release leachable constituents adjacent to the pulp. Nonetheless, adequately polymerized composites are relatively biocompatible because they exhibit minimal solubility, and unreacted species are leached in very small quantities. From a toxicological point of view, these amounts should be too small to cause toxic reactions. However, from an immunological point of view, under extremely rare conditions, some patients and dental personnel can develop allergic responses to these materials.

The most noted biocompatibility issue related to composite resin is the release of bisphenol A (BPA) from composites based



• **Figure 5-24** Placement time required for posterior amalgam, composite, and ceramic and composite inlay restorations. (Data from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*, York, UK, 2001, National Health Service Centre for Reviews and Dissemination, University of York.)

TABLE 5-6 Comparison of Average Time (Minutes) Required for Initial (I) and Replacement (R) Restorations

Restoration Type	AMALGAM		COMPOSITE		COMPOSITE AND CERAMIC INLAY	
	I	R	I	R	I	R
Class I	11	11	15	16	34	34
Class II	15	13	24	24	41	40
MOD: mesio-occlusal-distal	19	19	29	31	45	45
Cusp replacement with pins	25	26	33	34	44	44

I, Initial restoration; R, replacement restoration.

Adapted from Chadwick BL, Dummer PMH, Dunstan F, et al: *The Longevity of Dental Restorations: A Systematic Review*, York, UK, 2001, National Health Service Centre for Reviews and Dissemination, University of York.

on *bis*-GMA. BPA, a precursor of *bis*-GMA and an impurity in composite resin, has been shown to be a xenoestrogen, a synthetic compound that mimics the effects of estrogen by having an affinity for estrogen receptors. This estrogenicity of BPA was first reported in a clinical study in 1996, where BPA was collected in saliva after 1 hour of sealant placement, with the conclusion that sealant application led to xenoestrogen exposure in children. This led to a deluge of follow-up examinations to determine the validity of these results.

Studies have confirmed the release of BPA from composite resins, but the influence of BPA on the hormone balance is still in question. Additional information on the biocompatibility of restorative materials and the effect of BPA is presented in [Chapter 17, Estrogenicity and Systemic Reactions](#).

Finishing and Polishing of Composites

The term *finishing* usually refers to the process of adapting the restorative material to the tooth (e.g., removing overhangs and shaping occlusal surfaces that often leave behind irregular surfaces), whereas *polishing* refers to removing surface irregularities to achieve the smoothest possible surface. Residual surface roughness can encourage bacterial growth, which can lead to a myriad of problems, including secondary caries, gingival inflammation, and surface staining. The best possible surface finish is produced by placing a smooth matrix strip against composite resin during polymerization. However, achieving proper contours and margin adaptation is often difficult without some amount of finishing because the plastic strip does not yield with the convex and concave features like the tooth surfaces.

The mechanisms of finishing and polishing are discussed in [Chapter 16, Mechanics of Abrasive Procedures](#), along with the types of instruments used in dentistry. This segment will concentrate on the factors influencing the finish and polish of composite restoration: (1) environment, (2) delayed versus immediate finish, (3) the types of materials and instruments, and (4) postpolishing procedures.

Environment

Some advocates say that finishing in a dry field with the finishing equipment mounted on a slow-speed handpiece allows for better visualization of the restoration margins. However, studies have shown that a dry polishing technique results in an increase in marginal leakage, possibly because of heat production. Other studies have shown that structural and chemical changes occur on the surfaces of restorations as a result of a dry environment. In contrast, still other research has reported that the dry-polishing technique has no effect on the hardness or surface structure. As with many dental procedures, grinding and finishing are best accomplished in moderation. The clinician should finish the restoration in an environment where the margins are clearly discernible and where minimal heat is generated. Excessive heat results in smearing of the surface and depolymerization. Water-cooling during grinding and finishing should ensure a standard surface quality.

Elapsed Time Between Curing of the Composite and Finishing and Polishing

The elapsed time between curing and finishing of the composite may also have an effect on surface characteristics and resistance to leakage that develop. Some advocate delaying the

finishing of composite restorations for up to 24 hours because polymerization is incomplete at placement, although composite manufacturers recommend that finishing be accomplished shortly after placement. Studies have shown that delayed finishing can actually increase marginal leakage and has no effect on surface characteristics compared with immediate finishing. Also, delayed finishing has a minimal effect on hardness. Thus for all practical purposes, almost all composite restorations should be finished and polished shortly after placement during the same appointment, although the finishing should be delayed for approximately 15 min after curing.

Types of Materials and Instruments

A variety of materials and instruments can be used to finish and polish composite restorations. The use of a scalpel blade or any thin, sharp-edged instrument to remove flash on the proximal areas is recommended. However, this is a very risky procedure, especially if the trimming procedure involves shearing in a direction toward the composite and away from the gingival margin, which can lead to localized debonding and leakage. Trimming forces should be applied either parallel to the margin or toward the gingival tissue. Coarse to ultrafine aluminum-oxide discs can be applied to areas with difficult access around the proximal surfaces or in embrasures. Tungsten-carbide burs or fine diamond tips can be used to adjust occlusal surfaces and blend the composite to the surfaces of the teeth. Several studies in the literature have rated many of these systems as to their effect on surface smoothness and microleakage. Currently, aluminum-oxide discs produce the best surface, while also inducing minimal trauma. Other systems include resin-finishing instruments that use fine and extrafine polishing pastes, silicone-based systems, and silicon-carbide-impregnated polishing brushes and points. Although high stresses may be associated with surface grinding and polishing, a recent study has shown that the type of polishing system used does not significantly affect the development of microleakage.

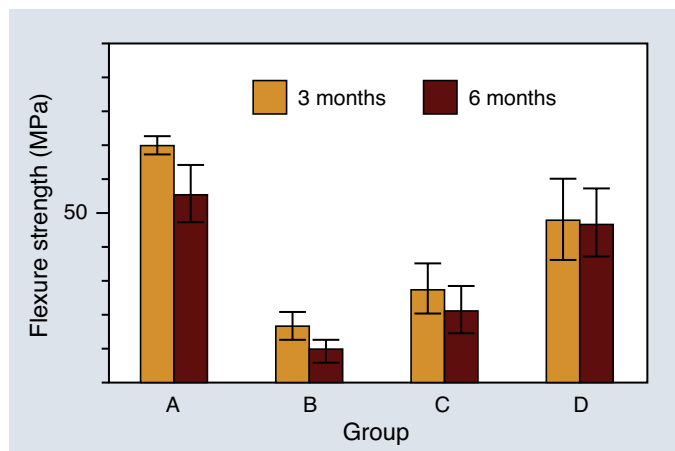
Surface Coating and Sealing

An important step in finishing and polishing is the application of a bonding agent or a surface sealer. There has been extensive documentation that the finishing (and possibly polishing) process is detrimental to composite surfaces in that surface microcracks are introduced, and the highly polymerized outer surface of the resin composite material is removed. Application of a penetrating surface sealer or a low-viscosity resin with little or no filler ensures that surface porosities are filled and microcracks sealed. Studies have shown that this “rebonding” technique also significantly decreases microleakage by improving the marginal seal of restorations.

Repair of Composites

Composites can be repaired by replacing lost material. This is a useful procedure for correcting defects or altering the contours on existing restorations. The procedures for adding new material differ depending on whether the restoration is freshly polymerized or an older restoration.

When a restoration has just been placed and polymerized, this restoration may still have an oxygen-inhibited layer of resin on the surface. The addition of new composite can be made directly



• **Figure 5-25** The influence of the method of composite repair on strength. Flexural strength after storage in distilled water at 37 °C for 3 and 6 months. **A**, Original, unbroken samples serving as a control. **B**, Repair without first acid-etching. **C**, Repair after acid-etching and the application of an unfilled resin. **D**, Repair after toluene/silane treatment to soften the broken surfaces and facilitate permeation by new monomer. (Adapted from Söderholm K-J: Flexure strength of repaired dental composites. *Scand J Dent Res* 94:364–369, 1986.)

to this layer because this represents, in essence, an excellent bonding substrate. Even after the restoration has been polished, adding more material can still repair a defect. A restoration that has just been cured and polished may still have about 50% of unreacted methacrylate groups to copolymerize with the newly added material.

As the restoration ages, fewer and fewer unreacted methacrylate groups remain, and greater crosslinking reduces the ability of fresh monomer to penetrate the matrix. The strength of the bond between the original material and the new resin decreases in direct proportion to the time that has elapsed between polymerization and the addition of the new resin. Furthermore, polished surfaces expose filler surfaces that are free from silane. Thus the filler surface area does not chemically bond to the new composite layer. Even ideally—that is, with the addition of a silane-bonding agent to the surface before the addition of new composite—the strength of repaired composite is less than half the strength of the original material (Figure 5-25).

Even though repair is essential to the overall longevity of composite restorations, there are very few reports of formal investigations or long-term trials concerning composite repair. Two- to 3-year clinical results have been reported showing good outcomes for repairs or the resealing of marginal defects, and a 7-year recall reinforced the use of a conservative repair strategy. A survey of general practitioners found that half always repair defective composite margins adjacent to enamel, but most replace a restoration if the defective margin is adjacent to dentin. Thus the repair of composite restorations with defective margins adjacent to enamel is becoming the standard of care.

Composite-Based Indirect Restorations

Composite materials can be used to make direct restorations extraorally and fix to prepared teeth with a composite-based bonding agent called *resin cement* (Chapter 7, Resin Cements). Two noted applications are resin veneers and composite inlays and onlays.

Composite Resin Veneers

Originally, resin veneering materials were heat-polymerized polymethylmethacrylate, which were improved subsequently by the addition of fillers and crosslinking agents. Microfill materials that use high-molecular-weight dimethacrylates as resin matrices have created renewed interest in resin-veneered metal restorations. These resins are polymerized using visible light or a combination of heat and pressure. In general, these new microfill resins have physical properties superior to those of the original unfilled resin.

The first resin veneers were mechanically bonded to metal substrates using wire loops or retention beads. Recent improvements in bonding mechanisms have included micromechanical retention created by acid etching the base metal alloy and the use of chemical bonding systems such as 4-META, phosphorylated methacrylate, epoxy resin, or silicon dioxide flame-sprayed to the metal surface, followed by the application of a silane coupling agent (silicoating).

Prosthetic resin-veneering materials have several advantages and disadvantages compared with ceramics. The advantages include ease of fabrication, predictable intraoral reparability, and less wear of opposing teeth or restorations. The drawbacks include low proportional limit and pronounced plastic deformation, which contribute to distortion on occlusal loading. Therefore the resin should be protected with metal occlusal surfaces whenever feasible. Leakage of oral fluids and staining below the veneers, particularly those attached mechanically, are caused by dimensional changes from water sorption, heating, and cooling. Surface staining and intrinsic discoloration tend to occur with these resins.

Resins are also susceptible to wear during toothbrushing. Thus instructing the patient on proper cleaning procedures using a soft toothbrush and mild abrasive toothpastes is necessary. Resin-veneered metal restorations are not suitable for use as removable partial denture abutment retainers, where the clasp arm engages an undercut on the veneered surface, because the resin is not as wear resistant as porcelain.

Resin composites can also be used as a conservative alternative to conventional prosthodontic restorations, such as veneers for masking tooth discoloration or malformation. The resins are used as preformed laminate veneers, in which resin shells are adjusted by grinding, and the contoured facing is bonded to tooth structure using the acid-etching technique with either chemical-activated, visible-light-activated, or dual-cured resin cements. Resins used to cement indirect restorations, veneers, and prosthetic devices are similar to flowable restorative resins but are adjusted to match the needs of luting applications.

Indirect Posterior Composites

Composites for the fabrication of onlays and inlays are polymerized externally, and then luted to the tooth with a composite-base cement. Indirect composite inlays or onlays reduce wear and leakage and overcome some of the limitations of resin composites. Several different approaches to resin inlay construction have been proposed: (1) the use of both direct and indirect fabrication methods; (2) the application of light, heat, pressure, or a combination of these curing systems; and (3) the combined use of hybrid and microfill composites.

The fabrication process for direct composite inlays first requires the application of a separating medium (e.g., agar solution or glycerin) to the prepared tooth. The restorative resin pattern is then formed, light-cured, and removed from the preparation. The rough inlay is then exposed to additional light for approximately 4 to 6 min or heat at approximately 100 °C for 7 min, after which

the preparation is etched, the inlay is cemented into place with (typically) a dual-cured resin, and then it is polished.

Composite systems are also available as indirect products. Indirect inlay resins require an impression and a dental laboratory technician to fabricate the inlay. In addition to conventional light- and heat-curing methods, laboratory processing may employ heat (e.g., 140 °C) and pressure (e.g., 0.6 MPa for 10 min). The potential advantage of these materials is that a significantly higher degree of polymerization is attained, which improves physical properties and resistance to wear. Because the polymerization is completed before placement into the prepared teeth, there are no shrinkage-induced stresses, and bond failures are reduced, which reduces the potential for leakage. Furthermore, these resins are repairable in the mouth and are not as abrasive to the opposing tooth structure as ceramic inlays.

Laboratory studies support these expected advantages: for example, a recent review revealed that the annual clinical failure rates in class I and II posterior stress-bearing cavities are the same for composite inlays as for amalgam restorations (1.9%), somewhat superior to those for direct composites (3.6%), and only slightly (but not significantly) inferior to cast gold inlays and onlays (1.4%). However, the technique sensitivity for indirect resin restoration systems remains high, and their appropriateness as a substitute for amalgam or cast restorations in *all* posterior applications is not clear, even though the esthetics are appealing.

Selection Criteria for Posterior Composites

Not all patients should be considered as candidates for these posterior restorations. The primary indication for using direct posterior composites in place of amalgams is esthetics. Unless the patient's esthetic demands are high, there are minimal advantages to using resin restorations in posterior regions. Often the disadvantages, coupled with the difficulty in manipulation, far outweigh the benefits. Other indications might include the need for conservative preparations along with conservation of tooth structure. Because composite restorations do not depend on mechanical undercuts for retention, the concepts of resistance form and retention form do not really apply to resin preparations. However, because of their inferior physical properties, composites should not be used for cuspal coverage or for large restorations exceeding one-third the buccolingual width of the tooth. If possible, the occlusal load should always be borne by sound tooth structure and never by resin. Because wear is also an issue, posterior composites should not be placed in patients experiencing parafunctional habits. Another lesser indication is the use of composites to minimize thermal conduction. Because amalgam is metallic, the material tends to conduct heat more rapidly, leading to tooth sensitivity

and pain. The placement of composites or ceramics, which are good thermal insulators, often reduces this occurrence.

Photocuring Training, Evaluation, and Process Management

In order to reach a high degree of cure, light-cured resins must receive sufficient energy at the appropriate wavelengths. The light energy delivered to the composite is dictated by the operator technique of focusing light on the restoration, the type of curing light, and the location of the restoration, and the energy needed for proper curing depends on the type of resin used. Clinicians may have dental radiometers to measure the irradiance at the emitting tip of a curing light but might not be certain if sufficient energy has been delivered to the restoration to reach an adequate cure level and depth of cure.

The “MARC” (an acronym for “managing accurate resin curing,” BlueLight Analytics Inc., Halifax, NS) device and training system shifts the paradigm away from measuring the average irradiance of a curing light and only including the wavelengths and energy actually received by the resin being polymerized. The MARC device combines precise laboratory spectral technology with clinically relevant measuring conditions within prepared dentiform teeth in a mannequin head. Spectrum-corrected sensors inside the dentiform teeth are attached to a laboratory-grade spectroradiometer embedded within the manikin's head to record the light received from curing units. Output from the spectrometer is fed into a laptop computer, where custom software provides real-time and accumulated comparison data: spectral irradiance, total energy delivered over a given exposure duration, and the estimated exposure duration needed to deliver a specified energy dosage.

In addition to providing real-time feedback to judge when adequate photoenergy has been delivered, the MARC device can also be used as a training aid for performing optimal photocuring in clinics. The effect of minor alterations in tip distance and angle and movement during exposure is displayed in real time, and the ultimate consequence in terms of altered energy delivered is determined. The device can also be used to determine the ability of various lamps to deliver adequate energy levels between different tooth locations.

Acknowledgment

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- The author discusses a complete array of composite systems, with emphasis on clinical applications. The book combines the science of dental polymers with discussions of clinical applications.
- Alvanforoush N, Palamara J, Wong RH, et al: Comparison between published clinical success of direct resin composite restorations in vital posterior teeth in 1995–2005 and 2006–2016 periods, *Aust Dent J* 62:132–145, 2017.
- Boaro LCC, Gonçalves F, Guimarães TC, et al: Polymerization stress, shrinkage and elastic modulus of current low-shrinkage restorative composites, *Dent Mater* 26:1144–1150, 2010.

This investigation found that not all composites that claimed “low-shrinkage” exhibited reduced polymerization shrinkage. It was also concluded that in order to effectively reduce polymerization stress [not just shrinkage], a low post-gel shrinkage must be accompanied by a relatively low elastic modulus.

Chen M-H: Update on dental nanocomposites, *J Dent Res* 89:549–560, 2010.

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Full Selected Readings for this chapter can be found on www.expertconsult.com.

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Selected Readings (Web version)

Useful Websites

The Biomaterials Network: <https://biomat.net/site2/>
 Clinicians Report: <https://www.cliniciansreport.org/>
 Dental Advisor: <http://www.dentaladvisor.com/>
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A host of review papers are presented on many aspects of dental composite chemistry, systems usage, dentin bonding agents, and microleakage.

Albers H: *Tooth-Colored Restoratives: Principles and Techniques*, 9th ed, Hamilton, ON, 2002, BC Decker.

The author discusses a complete array of composite systems, with emphasis on clinical applications. The book combines the science of dental polymers with discussions of clinical applications.

Alvanforoush N, Palamara J, Wong RH, et al: Comparison between published clinical success of direct resin composite restorations in vital posterior teeth in 1995–2005 and 2006–2016 periods, *Aust Dent J* 62:132–145, 2017.

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Bowen RL: Dental filling material comprising vinyl-silane treated fused silica and a binder consisting of the reaction product of bisphenol A and glycidyl methacrylate 112, Washington, DC, 1962, US Patent 3,006, US Patent and Trademark Office.

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6

Bonding and Bonding Agents

OUTLINE

Historical Background
Mechanisms of Adhesion
Acid-Etch Technique
Process and Procedural Factors

Dentin-Bonding Agents

Luting Agents

Applications in Orthodontic, Endodontic, and Preventive Dentistry

KEY TERMS

Acid-etching/acid-etch technique The process of cleaning and roughening a solid surface by exposing it to an acid and thoroughly rinsing the residue to promote micromechanical bonding of an adhesive to the surface.

Adhesion A molecular or atomic attraction between two contacting surfaces promoted by the interfacial force of attraction between the molecules or atoms of two different materials. Adhesion may occur as chemical adhesion (formation of covalent bonds, hydrogen bonds, or polar bonds via van der Waals attraction), mechanical adhesion (structural interlocking), or a combination of both types.

Cement/cementing Substance that hardens from a viscous state to a solid union between two surfaces. For dental applications, cements act as a base, liner, restorative filling material, or adhesive to bond devices and prostheses to tooth structure or to each other. See also *Luting agent*.

Contact angle Angle of intersection between a liquid and a surface of a solid that is measured from the solid surface through the liquid to the liquid–vapor tangent line originating at the terminus of the liquid–solid interface; used as a measure of wettability, whereby absolutely no wetting occurs at a contact angle of 180 degrees and complete wetting occurs at an angle of 0 degrees.

Dentin-bonding agent A thin layer of resin between conditioned dentin and the resin matrix of a resin-based composite restorative material.

Dentin conditioner An acidic agent that dissolves the inorganic structure in dentin, resulting in a collagen mesh that allows infiltration of an adhesive resin.

Hybrid layer An intermediate layer of resin, collagen, and dentin that is produced by acid-etching of dentin and infiltration of resin into the conditioned dentin.

Luting agent A viscous, cement-like material that also fills a gap between the bonded materials. It originally referred to nonadhesive agents only but now also includes adhesive agents.

Microleakage The flow of oral fluid and bacteria into the microscopic gap between a prepared tooth surface and a restorative material.

Obturation In endodontic dentistry, filling of a root canal completely and densely with a nonirritating hermetic sealing agent to prevent leakage.

Primer A hydrophilic, low-viscosity resin that promotes bonding to a moist substrate, such as dentin.

Resin tag Extension of resin that has penetrated into etched enamel or dentin. Resin tags form micromechanical interlocks analogous to screw threads.

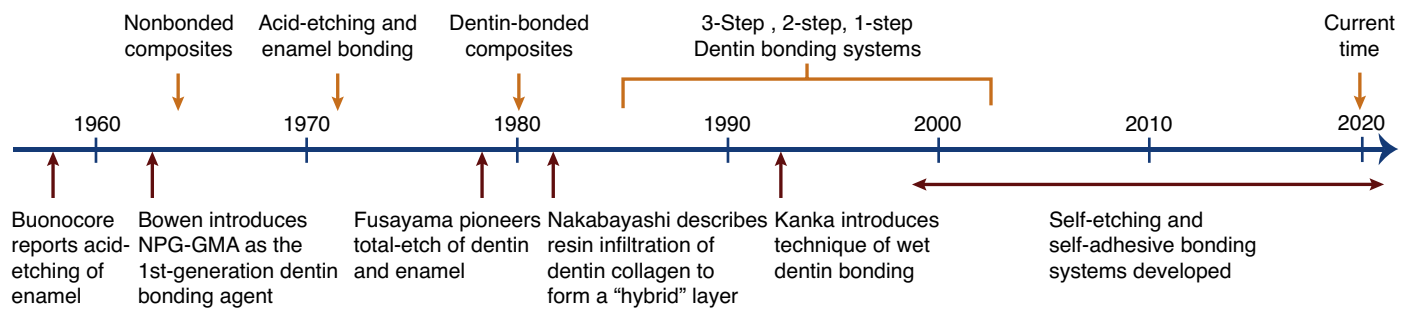
Smear layer Poorly adherent layer of ground dentin produced by cutting a dentin surface; also, a tenacious deposit of microscopic debris that covers enamel and dentin surfaces that have been prepared for a restoration.

Bonding and **adhesion** comprise a complex set of physical, chemical, and mechanical mechanisms that allow the attachment and binding of one substance to another. A dental bonding system performs three essential functions: (1) provides resistance to separation of an adherend substrate (i.e., enamel, dentin, metal, composite, ceramic) from a restorative or **cementing** material; (2) distributes stress along bonded interfaces; and (3) seals the interface via adhesive bonding between dentin and/or enamel and the bonded material, thus increasing resistance to **microleakage** and decreasing the risk for postoperative sensitivity, marginal staining, and secondary caries. The science of adhesion has been covered in [Chapter 2, Adhesion and Bonding](#). In this chapter, only those principles needed to understand dental bonding are discussed.

Historical Background

In 1949, Oskar Hagger, at the De Trey division of Amalgamated Dental, developed the first dental adhesive for dentin, Sevrित्रon Cavity Seal. This system comprised glycerophosphoric acid dimethacrylate, which should have made it a self-etching adhesive for both enamel and dentin by the discussion later. However, this product had very limited clinical durability because of the large interfacial stresses caused by the high polymerization shrinkage stress and high thermal expansion of the unfilled methacrylate-based resins used at the time.

Later, Michael Buonocore investigated the use of strong acids and discovered that phosphoric acid provides superior enamel etching,



• **Figure 6-1** Major turning points and events in dental bonding technologies.

and it is still in use today. As shown in [Figure 6-1](#), Buonocore's discovery of **acid-etching** led to the ability to produce clean, high-energy, roughened enamel surfaces capable of establishing a durable micromechanical retentive interface with resin-based **cements** and restorative materials, which launched the current era of adhesive dentistry. This led to burgeoning growth in the development of adhesive materials and bonding techniques, as summarized in [Figure 6-1](#) and discussed in detail in several later sections of this chapter.

CRITICAL QUESTION

Is good wetting of tooth structure by a dental adhesive adequate for long-term adhesive bonding of a restorative material?

Mechanisms of Adhesion

A means of true adhesion bonding (i.e., through chemical attraction and/or micromechanical interlocking) has been sought for decades and has recently been realized. For true adhesion of restorative materials to tooth structure, three conditions must be satisfied:

1. Sound tooth structure must be conserved
2. Optimal retention must be achieved
3. Microleakage must be prevented

Dental hard tissues and their environment are complex. However, the fundamental mechanism of adhesion to tooth structure can be regarded as an exchange by which mineral tooth material (hydroxyapatite) is replaced by synthetic resins. This process involves two steps: (1) removing hydroxyapatite to create micropores and (2) infiltration of resin monomers into the micropores and subsequent polymerization. As a result, **resin tags** form that micromechanically interlock (or interpenetrate) with the hard tissue. There may also be chemical interactions with the tooth substrate if monomers having acidic or chelating functional groups are present. In general, the following factors can play major or minor roles in achieving adhesive bonds:

1. Surface energy and wetting
2. Interpenetration (formation of a hybrid zone)
3. Micromechanical interlocking
4. Chemical bonding

Wetting is the essential first step for the success of all adhesion mechanisms. An adhesive cannot form micromechanical interlocks, chemical bonds, or interpenetrating networks with a surface unless it can form intimate contact with the surface, spread over it, displace air pockets, and penetrate by capillary attraction into any microscopic and submicroscopic irregularities. These conditions are, by definition, achieved if the adhesive wets the surface.

As explained in [Chapter 2, Contact Angle of Wetting](#), the wettability of a liquid on a solid can be characterized by the **contact**

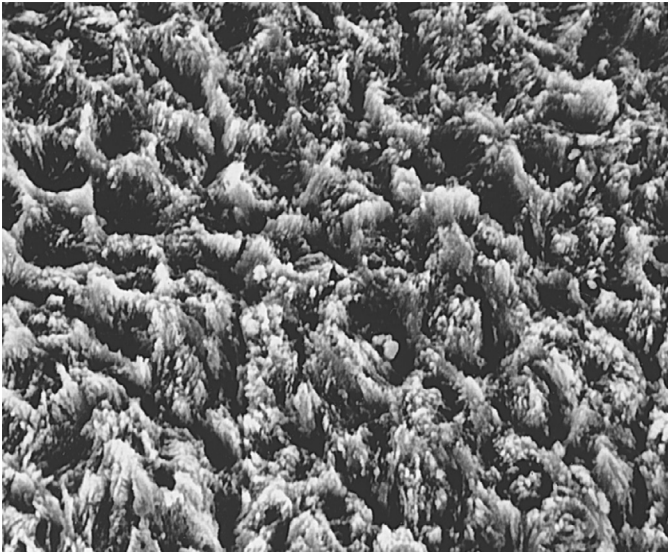
angle that forms between a liquid and solid, as measured within the liquid. Categories of wettability include "absolutely no wetting" (contact angle of 180 degrees), "mostly nonwetting" (>90 degrees), "mostly wetting" (<90 degrees), and absolute wetting (0 degrees). See [Figure 2-40](#) for a schematic illustration of wetting situations.

Wetting is essential for intraoral adhesion but is not sufficient to ensure durable bonding. To achieve strong bonding through the micromechanical interlocking mechanism, wetting monomers must intimately adapt to enamel and fill enamel surface irregularities and/or infiltrate into a demineralized collagen network in dentin. Some acid monomers with a phosphate (e.g., phenyl-P) or carboxyl group (e.g., 4-MET) have the additional potential of forming chemical bonds with calcium in the residual tooth tissue. Specific monomers with these types of functional groups will be discussed later.

Generally, wettability can be enhanced by increasing the surface energy of the substrates (e.g., dentin, enamel, and synthetic materials such as ceramics). Because a clean, microroughened tooth surface has higher surface energy than unprepared tooth surfaces, organic adhesives are inherently able to wet and spread over such a surface unless a low-surface-tension material contaminates the surface before the adhesive can be applied. The **acid-etch technique**, by which contaminants are removed and microporosities are created, is widely used to generate high-energy tooth surfaces and promote wetting by adhesive monomers.

Acid-Etch Technique

Whenever both enamel and dentin tissues are mechanically cut, especially with a rotary instrument, a layer of loosely held debris and organic film known as a smear layer is left on their surfaces and prevents strong bonding. Different quantities and qualities of smear layer are produced by various cutting and instrumentation techniques, which play an important role in both restorative and endodontic treatments, as explained further in [Chapter 7, Clinical Manipulation](#). In dentin, the smear layer becomes burnished into the underlying dentinal tubules and lowers dentin permeability, which is a protective effect. However, it is also a very weakly cohesive material and thus detaches easily, consequently interfering with strong bonding. Thus various cleaning or treatment agents and procedures must be employed to remove the smear layer and expose the intact substrate for bonding. As explained in greater detail in the discussion that follows, acid-etching is used to remove the smear layer from both enamel and dentin. Alternatively, in dentin, the smear layer can be left partially in place and modified such that adhesive resins penetrate through it and bond to the intact dentin structures below.



• **Figure 6-2** Surface of etched enamel in which the centers of enamel rods have been preferentially dissolved by phosphoric acid. (Courtesy K-J Söderholm.)

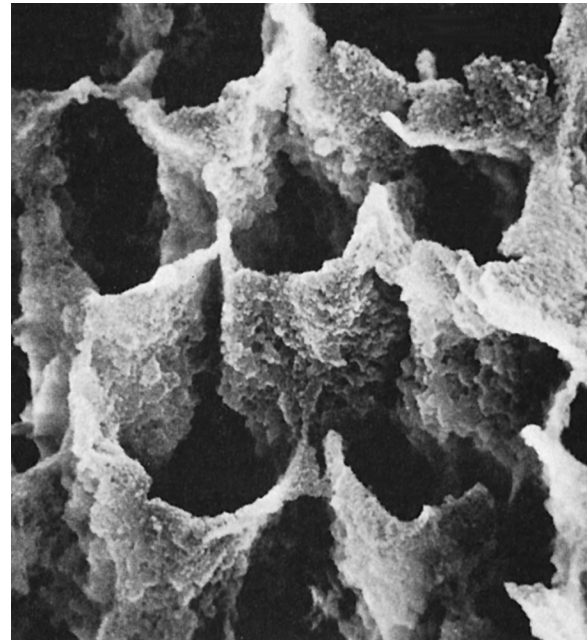
Enamel Etching

The first meaningful demonstration of intraoral adhesion was reported by Michael Buonocore (Figure 6-1). He etched enamel surfaces with various acids, placed an acrylic restorative material on the micromechanically roughened surfaces, and found a substantial increase in the resin–enamel-bond strength (~20 MPa). One of the surface-conditioning agents he used, phosphoric acid, is still the most widely used etchant for bonding to both enamel and dentin. Depending on the concentration, phosphoric acid removes the smear layer and about 10 microns of enamel to expose prisms of enamel rods and create a honeycomb-like, high-energy retentive surface (Figure 6-2). The higher surface energy ensures that resin monomers will readily wet the surface, infiltrate into the micropores, and polymerize to form resin tags (Figure 6-3). The pattern of etching enamel may vary from selective dissolution of either the enamel rod centers (type I etching), as shown in Figure 6-2, or the peripheral areas (type II etching), as indicated by the resin tags in Figure 6-3. In either case, the resin tags are about 6 μm in diameter and 10 to 20 μm in length.

Prior to the introduction of enamel acid-etching and the use of enamel-bonding agents, restorative materials were placed directly on the smear layer of the prepared tooth. It is evident that the apparent bond strength measured would be the cohesive strength of the smear layer to the tooth structure. As a result, debonding and leakage of oral fluids within the microscopic space between prepared teeth and restorative materials was an ongoing problem. Stronger and longer-lasting bonds result if the smear layer is removed because resins can then directly bond to the intact hard tissue.

Dentin Etching

As illustrated in Figure 6-1, dentin etching did not gain wide acceptance until Fusayama introduced the total-etch concept in 1979. For this method, both dentin and enamel are etched simultaneously, typically using 37% phosphoric acid. His study demonstrated that not only was retention substantially increased, but also pulp damage did not occur, as had been generally assumed. A subsequent study by Nakabayashi et al. revealed that hydrophilic resins can infiltrate



• **Figure 6-3** Scanning electron microscopy image of tags formed by the penetration of resin into etched areas of enamel. The resin was applied to the etched enamel, and enamel was then dissolved by acid to reveal the tags ($\times 5000$). (Courtesy K-J Söderholm.)

the surface layer of acid-demineralized collagen fibers produced in etched dentin and form a layer of resin-infiltrated dentin with high cohesive strength. Such a **hybrid layer** structure forms very strong resin bonds through the development of an interpenetrating network of polymer and dentinal collagen, together with numerous micromechanical interlocks at the resin–hybrid layer interface. By the early 1990s, dentin etching had gained worldwide acceptance. Because the total-etch technique usually involves etching with an acid followed by rinsing to remove the acid, this technique is also known as the *etch-and-rinse technique*.

Dentin etching is more technique sensitive than enamel etching because of the complexity of the dentin structure. Dentin consists of 50 vol% (volume percentage) of calcium phosphate mineral (hydroxyapatite), 30 vol% of organic material (mainly type I collagen), and 20 vol% fluid. Acid-etching removes hydroxyapatite almost completely from several microns of sound dentin, exposing a microporous network of collagen suspended in water. Whereas etched enamel must be completely dry to form a strong bond with hydrophobic adhesive resins, etched dentin must be moist to form a hybrid layer. The amount of water left in etched dentin is critical. If insufficient water is present, the collagen network will collapse and produce a relatively impermeable layer that prevents resin infiltration and subsequent hybridization. If too much water remains, resin infiltration cannot fully replace the water in the collagen network and, consequently, sets the condition for later leakage into those locations. Therefore a priming step is required to maintain a hydrated collagen network while removing excess water (see details in the following sections).

Process and Procedural Factors

Several aspects of the total-etch, etch-and-rinse, and related techniques are critical to the success or failure of bonding systems, as discussed next.

Etching Time

The optimal application time for the etchant may vary somewhat, depending on previous exposure of the tooth surface to fluoride and other factors. For example, a permanent tooth with high fluoride content may require a longer etching time, as do primary teeth. In the latter, increased surface conditioning time is needed to enhance the etching pattern on primary tooth enamel that is more aprismatic than permanent tooth enamel. Currently, the etching time for most etching gels is approximately 15 seconds. The advantage of such short etching times is that they yield acceptable bond strength in most instances while conserving enamel and reducing treatment time.

Rinsing and Drying Stage

Once the tooth is etched, the acid should be rinsed away thoroughly with a stream of water for about 20 seconds, and the water must be removed. When enamel alone is etched and is to be bonded with a hydrophobic resin (e.g., bisphenol-A glycidyl dimethacrylate [*bis*-GMA]–based resin; see [Chapter 5, Composition and Function](#)), it must be dried completely with warm air until it takes on a white, frosted appearance. Dentin, in contrast, cannot withstand such aggressive drying, which would cause bond failure because of the formation of impermeable, collapsed collagen fibers. In the total-etch technique, a **dentin-bonding agent** and **primer** must be used that are compatible with both moist dentin and moist enamel.

Cleanness of the Bonding Surfaces

To form a sound mechanical bond, etched surfaces must be kept free of contamination and sufficiently dry until the resin is placed. Although etching raises the surface energy, contamination can readily reduce the energy level of the etched surface. Reducing the surface energy, in turn, makes it more difficult to wet the surface with a bonding resin that may have too high of a surface tension to wet the contaminated surface. Thus even momentary contact with saliva or blood can prevent effective resin-tag formation and severely reduce bond strength. Another potential contaminant is oil that is released from the air compressor and transported along the air lines to the air–water syringe. If contamination occurs, the contaminant should be removed, and the surface should be etched again for 10 seconds.

Other Factors

The acid-etch technique was not widely used in the years immediately following its introduction ([Figure 6-1](#)). The principal reason was the inferior properties of the unfilled acrylic restorative materials used at that time. With those resins, high polymerization shrinkage (>6 vol%) and coefficients of thermal expansion in excess of 100 ppm/°C generated interfacial stresses sufficient to rupture the bond to etched enamel. After highly filled resin-based composites were marketed beginning in the mid-1960s, the acid-etch technique was “rediscovered.” Therefore, the choice of restorative materials also plays an important factor in the success of bonding.

CRITICAL QUESTION

What types of bond formation result from the use of dentin-bonding agents?

Dentin-Bonding Agents

Dental-bonding agents are designed to provide a sufficiently strong interface between restorative composites and tooth structure to withstand mechanical forces and shrinkage stress. The success of adhesives is dependent on two types of bonding:

1. Micromechanical interlocking, chemical bonding of the bonding agent with enamel and dentin, or both
2. Copolymerization of the bonding resin with the resin matrix of composite materials

Until the total-etch technique was adopted, bonding agents were used only to enhance the wetting and adaptation of resin to conditioned enamel surfaces. These bonding agents are made by combining various dimethacrylates used in resin composites (e.g., bis-GMA) with diluting monomers (e.g., triethylene glycol dimethacrylate [TEGDMA]; [Figure 6-4](#)) to control viscosity and to enhance wetting. These agents have little or no potential for chemical bonding, but they improve micromechanical bonding by optimal formation of resins tags within the etched enamel. Because enamel can be kept fairly dry, these rather hydrophobic resins perform well as long as they are restricted to enamel. They are generally called *enamel-bonding agents*.

Since the inception of the total-etch concept, in which both dentin and enamel are etched simultaneously, enamel-bonding agents have been replaced by the same systems that are used on dentin. The benefit is the ability to simultaneously bond resin to both enamel and dentin, leading to substantial improvements in bond strength. Numerous chemistries have been investigated, developed, and marketed in the search for adhesive systems that can produce strong, permanent bonds to dentin. Therefore the focus of discussion is on dentin-bonding agents.

As discussed in the section on adhesion in [Chapter 2, Bonding to Tooth Structure](#), and in an earlier section of this chapter, a successful dentin-bonding system must meet several requirements:

1. Adequate removal or dissolution of the smear layer from enamel and dentin
2. Maintenance or reconstitution of the dentin collagen matrix
3. Good wetting and efficient monomer penetration into the collagen matrix
4. Polymerization within the collagen mesh to form a hybrid layer
5. Copolymerization with the resin composite matrix

Composition of Dentin-Bonding Agents

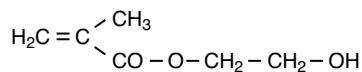
Irrespective of the number of components (see [Table 6-1](#)), a typical dentin-bonding system includes etchants, primers, solvents, resin monomers, initiators and inhibitors, reinforcing fillers, and sometimes other functional ingredients such as antimicrobial agents.

Etchants

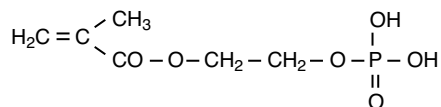
Enamel and dentin etchants are strong acids (pH = 1 to 2) used to remove smear layers and to dissolve the mineral phase so as to form micromechanical interlocking. A number of acidic agents have been used to produce the required microporosity. However, phosphoric acid, typically at 37%, produces consistent etching patterns while not damaging the pulp. Phosphoric acid concentrations greater than 50% result in the deposition of monocalcium phosphate monohydrate on the etched surface, which inhibits further dissolution. The etchant is usually supplied as an aqueous gel to allow precise placement over a specific area. Brushes are used to place the acidic gel, or the acid may be supplied in a disposable

Monomers with surface active and/or adhesive functional groups

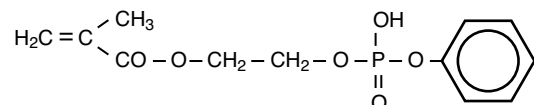
HEMA



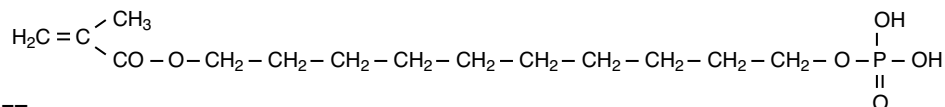
HEMA-phosphate



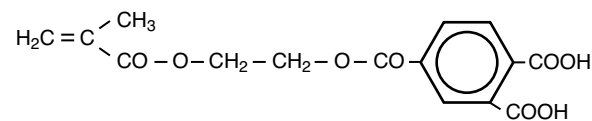
Phenyl-P



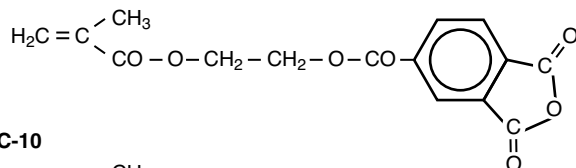
10-MDP



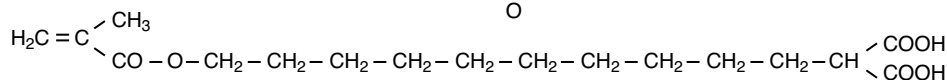
4-MET



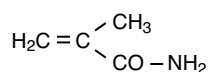
4-META



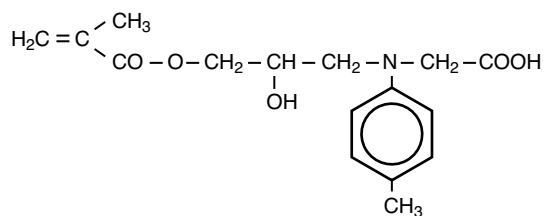
MAC-10



Methacrylamide

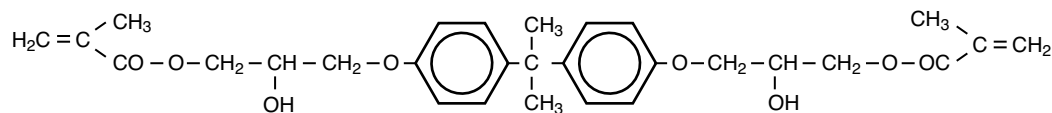


NPG-GMA

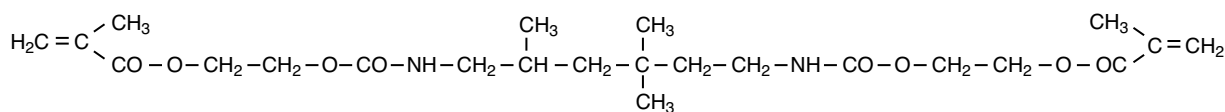


Monomers with crosslinking and copolymerizing functions

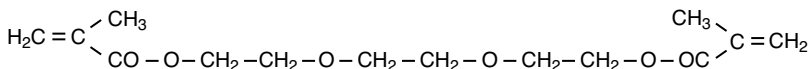
Bis-GMA



UDMA



TEGDMA



• **Figure 6-4** Structures of representative monomers used in enamel- and dentin-bonding agents.

TABLE 6-1 Classification of Dental Bonding Systems and Representative Examples of Commercial Products Currently Available for Clinical Use

ETCH AND RINSE		SELF-ETCH	
Three Step (4th generation)	Two Step (5th generation)	Two Step (6th generation)	One Step (7th generation)
1. Etch Apply for 15 s, rinse 15 s, gently air-dry, while keeping dentin moist.	1. Etch Apply for 15 s, rinse 15 s, gently air-dry while keeping dentin moist.	1. Etch and prime One application without rinsing, gently air-dry.	1. Etch, prime, and bond Apply 1–5 layers without rinsing, gently air-dry, light-cure.
2. Prime Apply 1–5 layers, gently air-dry.	2. Prime and bond Apply 1–5 layers, gently air-dry, light-cure.	2. Bond Apply one layer, gently air-dry, light-cure.	
3. Bond Apply one layer, gently air-dry, light-cure.			
REPRESENTATIVE PRODUCTS CURRENTLY MARKETING FOR CLINICAL USE			
Adper Scotchbond Multi-Purpose (3M ESPE) Syntac (Ivoclar Vivadent) DentASTIC All-Purpose (Pulpdent) GLUMA Solid Bond (Heraeus Kulzer) Optibond FL (Kerr)	DenTASTIC UNO (Pulpdent) Excite F VivaPen (Ivoclar Vivadent) iBond Total Etch (Heraeus Kulzer) One-Step and also One-step Plus (Bisco) Prime & Bond NT (Dentsply)	Adper Prompt (3M ESPE) AdheSE (Ivoclar Vivadent) All-Bond SE (Bisco) Clearfil SE Protect Bond (Kuraray) Nano-Bond (Pentron) One-Step Plus with/ Tyrian SPE (Bisco) Peak SE with Universal Bond (Ultradent)	AdheSE Universal (Ivoclar Vivadent) Adper Easy Bond Self Etch (3M ESPE) Adper Prompt L-Pop (3M ESPE) Clearfil S3 Bond (Kuraray) Futurabond DC (VOCO) G-Bond (GC), and XENO V (Dentsply) i-Bond Self Etch (Heraeus Kulzer)

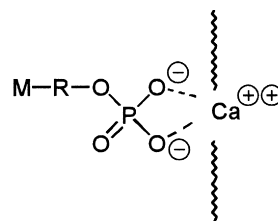
syringe from which it can be expressed onto enamel and dentin. During placement, it is important to be aware of the risk of air bubbles being introduced at the interface because the regions with air pockets will not be etched.

Primers

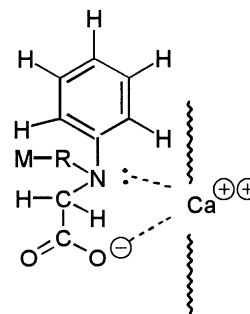
Dentin etching is highly technique sensitive because the demineralized collagen network readily collapses when dried. Therefore priming is necessary to maintain an expanded collagen network while removing residual water to allow for the infiltration of the hydrophobic adhesive monomer. Primers are solutions containing hydrophilic (water-loving) monomers dissolved in a solvent, such as acetone, ethanol, or water. Such monomers exhibit hydrophilic properties through phosphate, phosphonate, carboxylic acid, alcohol, or ester functional groups (Figure 6-4). For example, 2-hydroxyethyl methacrylate (HEMA) is a widely used primer monomer because of its high hydrophilicity (resulting from its -OH group) and solvent-like nature.

It was believed that dentin bonding could be achieved by forming chemical bonds between a primer and either the inorganic or the organic components of dentin, in particular, the Ca^{2+} within the hydroxyapatite mineral phases of dentin. Phosphate and carboxylic groups form chelation bonds with Ca^{2+} and, therefore, are expected to form such bonds during dentin priming, as has been found with carboxylate-based cements (Chapter 7, *Glass-Ionomer Cement*) and as illustrated in Figure 6-5, along with a bonding mechanism by amino-carboxylate functional groups. On the same molecule, there should be a polymerizable functional group, such as methacrylate, that can react with the resin adhesive and thereby form a chemical bond between the adhesive and dentin. This approach appeared in Hagger's dentin-bonding system, which was glycerophosphoric acid dimethacrylate with a typical M-R-X structure (Figure 6-6, A).

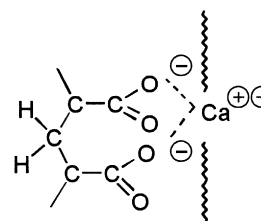
The design of such dentin-bonding agents is based on the successful model of silane coupling agents, as used to bond the inorganic filler to the matrix resin in composites (see Figure 5-4), to bond porcelain laminate veneers through resin cements to acid-etched enamel,



Phosphate-based bonding agent

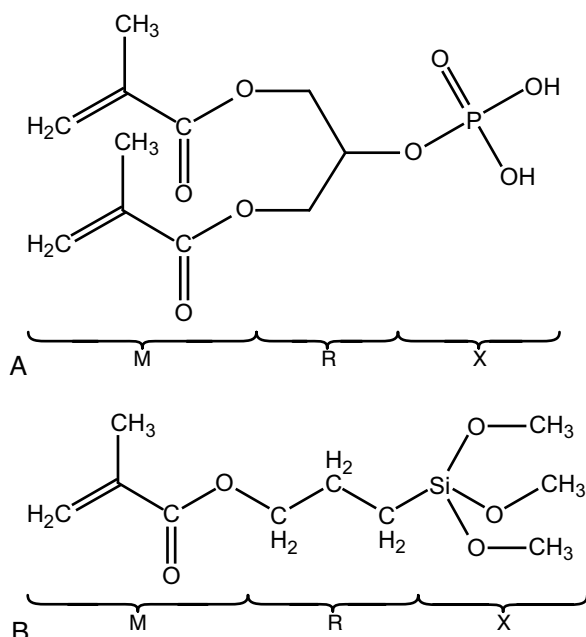


Amino-carboxylate-based bonding agent (NPG-GMA)



Carboxylate-based bonding agent (PAA)

• **Figure 6-5** Chemical bonding mechanisms to hard tooth tissues through calcium salt formation with monomers having adhesive functional groups. (Courtesy K-J Söderholm.)



• **Figure 6-5** M-R-X structures of dentin-bonding agents. **A**, Glycero-phosphoric acid dimethacrylate. The chemical adhesion or bonding mechanism of phosphoric acid is shown in [Figure 6-5](#). **B**, γ-Methacryloxypropyl trimethoxysilane. The surface interaction or bonding mechanism of the silane is shown in [Figure 5-4](#).

and to repair fractured porcelain with composites ([Chapter 10, Bonding of Resin to Dental Ceramics](#)). [Figure 6-6, B](#) shows a silane coupling agent presented as an M-R-X structure. X represents a group capable of chemically reacting with siliceous materials such as glass and silicate filler particles in composites, porcelain crowns and veneers, and/or the calcium ions (Ca^{2+}) in dental hard tissues. R is a spacer group that provides flexibility and mobility, and thus enhanced reactivity, for the M group after the X group has been immobilized by reaction at a surface. M represents an unsaturated methacrylate group or groups capable of copolymerizing with the other monomers of a resin cement or composite and thereby forming a chemical bond between the adhesive and dentin. Several compounds that are believed to possess these properties are shown in [Figure 6-4](#): NPG-GMA (a condensation product of *N*-phenyl glycine and glycidyl methacrylate and the first-generation dentin-bonding agent), polymerizable phosphates (e.g., 2-[methacryloyloxyethyl] phenyl hydrogen phosphate [phenyl-P] and 10-methacryloyloxydecyl dihydrogen phosphate [10-MDP]), and carboxylate compounds (e.g., 4-methacryloyloxyethyl trimellitic acid [4-MET], 11-methacryloyloxy-1,1'-undecanedicarboxylic acid [MAC-10], and 4-methacryloyloxyethyl trimellitic anhydride [4-META]). A number of phosphonic acid acrylates and bis(acrylamide), which are resistant to water degradation (hydrolysis), form a more durable, longer-lasting bond (e.g., AdheSE Primer; see [Table 6-1](#)). Also in this category are poly(alkenoic) acids as used in carboxylate and glass-ionomer cements, which are discussed later in this chapter and in more detail in [Chapter 7, Glass-Ionomer Cement](#).

Primer mixtures have a wide pH range because of the acidity of various functional monomers incorporated to promote bonding to the tooth structure. The rank of functional groups in their acidity is as follows: sulfonic acid > phosphonic > phosphoric >

carboxylic > alcohol. If the concentration of acidic monomers is increased in a HEMA base, a primer formulation may reach a pH (e.g., 1–2) low enough to remove smear layers and etch underlying dentin. If a primer has the ability to both etch and prime, it is categorized as a self-etching primer. For this purpose, acidic monomers are frequently used to formulate self-etching primers. Representatives of these are shown in [Figure 6-4](#): HEMA-phosphate, phenyl-P, 10-MDP, 4-MET, 4-META, and MAC-10.

In spite of theoretical evidence that chemical bonding to tooth structure is possible, no convincing experimental evidence has yet been validated to prove that significant chemical bonding occurs between dentin adhesives and tooth structure under intraoral conditions. Rather, the adhesive functional groups facilitate surface cleaning and etching and the development of micromechanical interlocking and monomer penetration of dentin to form a hybrid layer of molecular entanglements between collagen and polymer, as described previously.

Solvents

Solvents also play important roles in priming systems. The most commonly used solvents are water, ethanol, and acetone. In addition to enhancing the wetting of hydrophilic dentin, each solvent is chosen to make a specific contribution to improve bond adhesion. Water can ionize acidic monomers as well as re-expand the collapsed collagen network and make a hybrid layer possible. Ethanol and acetone have better miscibility with relatively hydrophobic monomers, and their “water-chasing” ability facilitates water removal. Removing solvent before proceeding to the next step is critical for a durable bond.

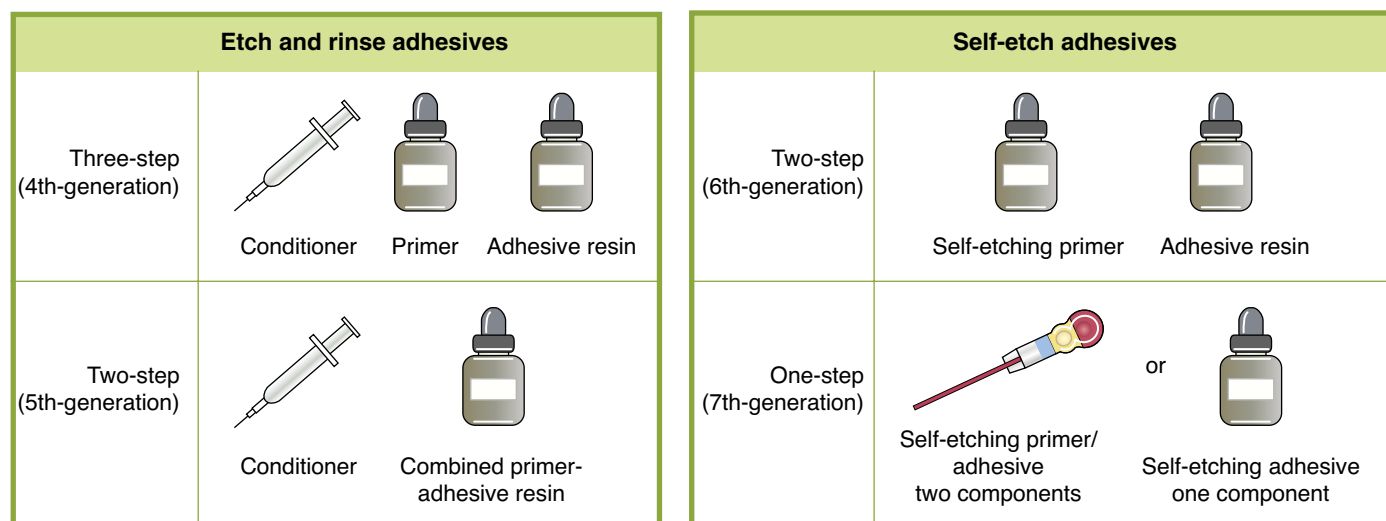
Adhesives

For dentin bonding, the primary purpose of adhesives is to fill the interfibrillar space of the collagen network, creating a hybrid layer with resin tags to provide micromechanical retention upon polymerization and serve as an intermediary bonding to the restorative materials made of hydrophobic resins. This function is similar to the role of enamel-bonding agents as an intermediate layer between the etched enamel and the resin-based restorative material. Likewise, the adhesive layers of a dentin-bonding system should also prevent fluid leakage along the restorative material's margin.

It is evident that adhesives need to be hydrophobic so that oral fluids will be repelled and not permeate through the intermediate layer. At the same time, adhesives require a certain hydrophilicity to diffuse into the hydrophilic primer-wetted dentin. To achieve these two conflicting requirements, adhesive resins are typically composed mainly of hydrophobic dimethacrylates, such as *bis*-GMA, TEGDMA, and urethane dimethacrylate (UDMA), and a small amount of a hydrophilic monomer such as HEMA. Monomers with phosphonic acid and methacrylamide functional groups could be added to improve resistance to hydrolytic degradation of the adhesives; however, the focus has mostly been on improving hydrolytic degradation of the one-step self-etching adhesives, which are discussed later.

Initiators

Similar initiator systems are used in both adhesives and restorative composites ([Chapter 5, Classification by Curing Method](#)). Polymerization can be initiated either through a photoinitiator system consisting of a photosensitizer (e.g., camphorquinone) and a co-initiator (e.g., tertiary amine), a self-cure system that includes a chemical initiator (e.g., benzoyl peroxide), or a dual-cure initiator system.



• **Figure 6-7** Classification of current adhesive systems according to van Meerbeek et al. (2003). (Adapted from Cardoso MV, et al: Current aspects on bonding effectiveness and stability in adhesive dentistry, *Aust Dent J* 56[S1]:31–44, 2011.)

Filler Particles

Nanometer-sized silica particles have been added to some adhesives to reinforce the adhesive and thereby produce higher bond strengths. However, the strengthening effect of the fillers in adhesives is uncertain because it is not clear whether these fillers can actually penetrate into the demineralized collagen networks because the interfibrillar space of the collagen networks is within the range of 20 nanometers (nm), whereas the nano-sized reinforcing filler particles are in the 40-nm range. The other reason for the addition of fillers is to effectively modify adhesive viscosity to a thicker, pastier consistency. When such an adhesive is applied to an etched dental surface, it yields a thicker bonding layer that can promote increased bond strength by preventing oxygen inhibition. Moreover, a thick adhesive layer can reduce shrinkage stress because it is more compliant, which relieves shrinkage-induced stresses, compared with restorative composites ([Chapter 5, Function of Fillers](#)).

Other Ingredients

Additional ingredients are used with dentin-bonding agents for a variety of specific purposes. Examples include the following: glutaraldehyde (Probond, Dentsply, York, PA) is added as a desensitizer. The monomers 12-methacryloyloxydodecylpyridinium bromide (MDPB; Clearfil Protect Bond, Kuraray America, New York, NY) and paraben (Adper Prompt L-Pop, 3M ESPE, St. Paul, MN) are used as antimicrobials. Fluoride (Prime & Bond NT, Dentsply, York, PA) is added to prevent secondary caries. Benzalkonium chloride (e.g., Etch 37, Bisco, Schaumburg, IL) and chlorhexidine (e.g., Peak LC Bond Resin, Ultradent Products, South Jordan, UT) are used to prevent collagen degradation. In laboratory studies, both benzalkonium chloride and chlorhexidine have been shown to prevent protease enzymes (matrix metalloprotease enzymes or proteins [MMPs]) from being activated and subsequently denaturing the hybrid-layer collagen. Unfortunately, however, clinical studies have failed to show improved dentin-bond durability after treatment with these agents.

CRITICAL QUESTION

Why are dentin-bond-strength values so variable?

Properties of Bonding Agents

Bonding systems are often characterized by their bond strength to the intended substrates, the ability to provide a sealed tooth/restoration interface, and resistance to hydrolytic degradation. Hydrophilic monomers are incorporated into the system to improve bonding to the moist tooth structures.

Measurement of Bond Strength

Evaluation of the efficacy of dentin adhesives is generally based on the bond strength as determined by loading bonded test specimens in shear or in tension until fracture occurs. Such tests offer only indirect evidence of how the adhesive is likely to perform in vivo. Data published on bond strength for a given material often vary widely, with high standard deviations. This wide variance is better described by the coefficient of variation (standard deviation/mean) and is attributed to the inherent variations at the dentin surface, such as water content, the presence or absence of a smear layer, dentin permeability, orientation of the tubules relative to the surface, and differences in the in vitro test design and stress distribution adjacent to the interface. Although there is no agreement on the minimum strength necessary to provide successful bonding, 20 MPa or higher has been proposed as a reasonable goal.

Current dentin-bonding agents can have bond strengths high enough to shift the site of clinical failure from the interface to within the dentin adjacent to the restoration or, in some cases, within the restoration adjacent to the interface. Thus it is clear that the inherent bond strength is no longer the limitation in the effectiveness of bonded restorations. The limiting factor now appears to be, at least for large restorations, induced stresses generated during curing shrinkage within the resin-based composite itself. Several products with reduced interfacial polymerization stress have recently been introduced ([Chapter 5, Low Shrinkage Composites](#)), and means of further stress reduction are currently under investigation and should eventually eliminate this as a significant clinical problem.

Measurement of Microleakage

The degree of microleakage at the restoration–tooth interface can be monitored by the penetration of tracers and staining agents. As is true for bond strength testing, there is also a large variation in

leakage data, depending on the measurement technique and the manipulation during placement. Often, a good correlation does not exist between bond strength and microleakage. However, the newer low-stress products appear to be superior in inhibiting interfacial leakage between the conditioned tooth structure and adhesive resin.

Aging Effects and Degradation of the Hybrid Layer

The change of bond strength over time is a useful indication of clinical lifetime and can be evaluated by in vitro accelerated aging tests. Several investigations have found that the bond strength of three-step adhesive systems show little or no decrease in contrast to two-step adhesive systems that decrease significantly during a 4- to 5-year span. Research has also shown that peripheral bonding to etched enamel, which seals the resin bond from exposure to water, can significantly increase bond durability. Transmission electron microscopy (TEM) observations have shown that collagen fibrils in the hybrid layer degrade coincidentally with decreasing bond strength, suggesting that hybrid-layer degradation contributes to aging of dentin-bond integrity. As indicated in the earlier subsection on “other” bonding agent ingredients, this is likely caused by the activation of MMPs, which denature the hybrid-layer collagen.

Some in vitro studies offer a degree of predictability for certain clinical situations. For example, a durable dentin bond can be expected if enamel bonding is used to seal all cavity margins.

Another requirement for achieving lasting intraoral bonds is hydrolytic stability (resistance to chemical degradation by water). Enamel and dentin are hydrated, hydrophilic, and permeable to water. Even if an enamel or dentin surface is initially dried before applying an adhesive, inadvertent contamination and diffusion can easily result in water becoming strongly bound to both the hard tissue and the adhesive. Thus for an adhesive monomer to wet hard tooth tissue as well as form a durable bond in the moist environment of the mouth, it must be both hydrophilic for water compatibility and hydrolytically stable to ensure longevity.

CRITICAL QUESTION

Do bonding agents perform the same in bonding to enamel and dentin?

Classifications by Clinical Steps

When discussing dentin-bonding agents, it has become customary to describe the generations (first generation, second generation, etc.) of bonding agents that have led sequentially from the earliest, relatively ineffective materials to the current materials, which provide reliable functional bonds. This organization into generations of bonding agents is a somewhat artificial device to mark key advances in materials and techniques along a more-or-less continuous developmental pathway. Therefore this chapter uses a more logical and straightforward classification for contemporary adhesive systems based, rather, on their strategy of adhesion and the number of clinical steps involved. This classification was developed by van Meerbeek et al. As shown in Figure 6-7 and Table 6-1, it is based on two general approaches to etching, priming, and applying the bonding resin to dentin and enamel surfaces and further subdivided into the number of steps in the process. Thus the major categories of bonding systems are known as *etch-and-rinse* and *self-etch* systems, with two subcategories, each according to the number of clinical steps involved.

Etch-and-Rinse Adhesives

Three Step (Fourth Generation)

The long-established, highly reliable method in this category consists of three steps: (1) an acid-etchant application, (2) application of the

primer, and (3) application of the bonding resin. The primer contains hydrophilic functional monomers dissolved in an organic solvent such as acetone or ethanol, or water. The third step is the application of a hydrophobic resin, as mentioned earlier in the chapter.

Two Step (Fifth Generation)

A simplified method in this category combines the primer and adhesive resin into one application. This etch-and-rinse strategy is the most effective to achieve efficient and stable bonding to enamel. Etching, usually with a 30% to 40% phosphoric gel that is rinsed away, promotes the dissolution of enamel rods, creating porosities that are filled by a bonding resin through capillary action, and then followed by resin polymerization.

With dentin, bonding is more difficult and less predictable than with enamel because of the organic characteristics of dentin. In this case, phosphoric acid treatment exposes a collagen network that is nearly devoid of hydroxyapatite. Bonding occurs by diffusion and infiltration of the resin within the collagen mesh, forming a hybrid layer. After in situ polymerization, this hybrid layer provides micromechanical retention to the restoration. As explained earlier, true chemical-adhesive bonding is unlikely to contribute to bond strength because the monomers have only a weak affinity for collagen. Further, in the two-step category, hydrophilic and ionic monomers are combined, with the result that the bonded interface does not develop an all-hydrophobic resin layer, thus leaving the bond susceptible to water penetration and subsequent degradation, which greatly reduces bond durability.

Self-Etch Adhesives

Two Step (Sixth Generation)

This approach does not involve a separate etching step. In this case, an acidic monomer, which is not rinsed, is used to condition and prime at the same time. There are two types of self-etch adhesive: mild and strong. Strong self-etch adhesives have a low pH (<1) and have a bonding mechanism that resembles that of the etch-and-rinse adhesives. Mild self-etch adhesives (pH = 2) only partially dissolve the dentin surface, so a substantial amount of hydroxyapatite remains available within the hybrid layer. Specific carboxyl or phosphate groups of functional monomers can then chemically interact with this residual hydroxyapatite. Because this layer has some mineral content, the bond to dentin is better than that of etch-and-rinse adhesives. However, this interfacial zone can be more prone to hydrolytic degradation because the structure is more hydrophilic and thus subject to water intrusion. The dentin-bond durability of mild self-etch primer systems seems to be adequate.

One Step (Seventh Generation)

The simplified method in this category combines a dentin conditioner, primer, and bonding resin into a single step. Most one-step or “all-in-one” systems are delivered by a bottle, vial, or single-unit dose applicator, which is formulated as a single component. However, Adper Prompt L-Pop (Table 6-1) is a variation on this theme, in which two liquid components are packaged in separate “blister” compartments in a single dispenser. Bursting one blister causes the two components to blend and form a single component, which is then applied immediately using a brush that forms the handle of the blister pack. This version of one-step, two-component, self-etching primer–adhesive is illustrated in Figure 6-7.

One-step self-etch adhesives are an attractive approach for clinicians because of the reduced and less complex number of clinical steps required compared with multistep etch-and-rinse adhesives.

There is no need for rinsing or drying of the tooth structure because of the lack of an etch step. Because of this, numerous self-etch adhesive bonding agents have been introduced that expand this category for use with total-etch procedures (Adper Easy Bond Self-Etch; [Table 6-1](#)). These recently developed products have shown durability and versatility for use in an array of clinical applications. New phosphonic acid ether acrylates and cross-linking *bis*(acrylamide)s facilitate the preparation of self-etching enamel–dentin adhesives with improved storage stability.

Products in the one-step, self-etch category have undergone limited clinical experience but are showing comparable performance and durability to two-step self-etch and etch-and-rinse products.

These four categories are described in [Table 6-1](#), which also provides typical application instructions and examples of representative commercial products for each category. Over the last several years, the availability of one-step products has been increasing, and they are replacing earlier versions in the three-step and two-step categories.

CRITICAL QUESTION

Can a single luting agent be used for cementation of indirect restorations in all clinical scenarios?

Luting Agents

For many years, retention of indirect restorations could only be attained by the use of favorable tooth preparations and by micro-mechanical interlocking into irregularities present on the surface of the restoration and the tooth, without adhesive bonding, as discussed in this chapter. This type of material is known as a luting agent. The most notable materials in this category are zinc phosphate and zinc oxide–eugenol (ZOE) cements ([Chapter 7, Zinc Oxide-Based Cements](#)). These lack adhesion and chemical bond formation with tooth structure and, thus, exhibit low bond strength to dentin. The introduction of adhesive bonding to enamel and dentin completely changed the procedure of affixing indirect restorations. A number of adhesive bonding materials are available for bonding prostheses, including polycarboxylate cements, glass-ionomer cements, resin-modified glass-ionomer (RMGI) cements, and resin cements, which are described in more detail in this section and in [Chapter 7, Combination Cements](#). Traditionally, the terms *luting* and *cementing* refer to the use of nonadhesive materials for retaining prostheses, whereas *bonding* refers to the use of adhesive bonding materials. The distinction has faded in the literature; the use of adhesive bonding medium is also called *luting*. This section will concentrate on their bonding mechanism and recent developments in adhesive bonding agents.

Resin cements are low-viscosity resin-based composites that can bond to various substrates, including tooth structure, resin composites, metal alloys, porcelain, and other ceramics. For cementation of indirect restorations, where most of the tooth structure is dentin, resin cements have shown better mechanical properties compared with others, such as zinc phosphate cement. Resin cements can follow the application of dentin-bonding agents, or not, when bonding to tooth structure. The former can be considered either as an etch-and-rinse adhesive resin cement or as a self-etch adhesive resin cement, according to its bonding-agent system. The latter is a self-adhesive resin cement. In vitro studies have reported better enamel-bonding performance for non–self-adhesive resin cements compared with self-adhesive cements. Self-adhesive resin cements

do not show significant infiltration into dentin, but apparently some type of chemical interaction occurs between the calcium in hydroxyapatite and the cement monomer functional groups. For cementation of all-ceramic restorations, resin cement is the material of choice. Preparation of an all-ceramic restoration can include, but is not limited to, sandblasting, application of hydrofluoric acid for etching, silanization, or application of a ceramic primer to improve bond strength. Bonding to ceramic substrates is discussed in [Chapter 10, Bonding of Resin to Dental Ceramics](#).

CRITICAL QUESTION

Why are glass-ionomer cements also used as restorative material for class V erosion lesions?

When an acid-soluble calcium aluminofluorosilicate glass powder is mixed with an aqueous solution of polyacrylic acid or analogous polyacid (also known as *ionomers*), Ca^{2+} and Al^{3+} ions released from the powder react with the carboxylic acid ($-\text{COOH}$) of polyacids and crosslink polyacid to form a solid. The solid is known as *GIC* and can be used to make restorations. The surface of a freshly mixed GIC should appear wet and rich in carboxylic acids. These carboxylic groups will interact strongly with surface Ca^{2+} ions in enamel or dentin, resulting in chemical adhesion to tooth structure as the GIC sets. This chemical adhesion may also be beneficial in terms of resistance to hydrolytic degradation. This behavior qualifies GIC as a self-adhesive cementing medium and restoration.

A short treatment with polyacrylic acid can clean the tooth surface and remove the smear layer, exposing collagen fibrils to a depth of about 0.5 to 1 micron, which improves the micromechanical bonding of the GIC to dentin surfaces. Most of the current GICs have been modified with polymerizable acrylate monomers and are referred to as *RMGIs*. They contain a light-curable acrylic resin that provides for rapid polymerization at and near the surface, and they bond using the same bonding mechanisms as nonresin glass ionomers.

Clinical longevity depends not just on bond strength but also on dislodging forces. Composite restoratives undergo significant polymerization shrinkage ([Chapter 5, Cure Shrinkage and Managing Shrinkage Stress](#)), which creates stresses adjacent to the resin–dentin interface that can rupture dentinal bonds in all but the smallest restorations. Because glass ionomers generate low stresses on setting, they are well retained even in areas such as class V sites, where occlusal forces induce relatively little stress. They also have been used with somewhat limited success as pit and fissure sealants. However, because of the high stresses induced by intraoral forces in occlusal areas, a greater degree of dislodgment and fracture of the GIC sealants occurs in these sites. GICs are described in some detail in [Chapter 7, Glass-Ionomer Cement](#).

CRITICAL QUESTION

Why are self-adhesive cements currently not used to bond orthodontic brackets?

Applications in Orthodontic, Endodontic, and Preventive Dentistry

The procedures of acid-etching and adhesive bonding that provide a strong, durable bond between resin and tooth structure have also been the basis for dental procedures as diverse as orthodontic bracket bonding, endodontic sealers, amalgam bonding, and pit

and fissure sealants. Additional applications in the bonding of prostheses, porcelain laminate veneer bonding, and adhesive cements, including glass-ionomer restorative materials, will also be discussed in greater detail throughout the book but with particular emphasis in the chapters on composites, cements, amalgams, and ceramics.

Bonding Resins for Orthodontic Brackets

Orthodontic treatment with fixed appliances involves brackets and bands. Bands are flat metal bands that encircle teeth and are usually used on molars. Brackets are welded to bands or bonded to enamel and hold the wires that apply forces for tooth alignment. The development of bonding has contributed to a decrease in banding, even in posterior teeth. Various luting agents have been used in orthodontics, such as polycarboxylate cement, GIC, and RMGI cements. Contemporary bonding to enamel involves the following:

1. Prophylaxis of bonding surface
2. Etching with phosphoric acid gel or aqueous solutions
3. Rinsing with water
4. Drying with air
5. Application of sealant or primer
6. Bonding of brackets with resin cement
7. Light-curing the dual-cured or light-cured cement

Manufacturers do not recommend self-adhesive cements as luting agents for orthodontic fixed appliances. Self-adhesive cements have lower bond strengths to intact enamel in comparison with conventional orthodontic resin cements that require etching with phosphoric acid. However, self-etching systems have shown acceptable results for the bonding of orthodontic brackets.

In orthodontic treatment, bonding involves mainly enamel. Increasingly, adults are undergoing tooth alignment. This population has more amalgam restorations, porcelain-fused-to-metal (PFM) crowns, and all-ceramic crowns. Therefore bonding of brackets to those surfaces also plays an important role in orthodontic treatment. It is important that the bonding of brackets be reliable because replacing loose brackets is time-consuming and costly.

Several types of surface treatments can be used with restorative materials to increase bond strength. For example, roughening with a diamond bur and sandblasting enhance bonding, especially in the case of metals. These treatments create surface irregularities and increased surface area. This promotes micromechanical retention and chemical adhesion in the case of resins, such as those containing 4-META, 10-MDP, and others, as shown in Figure 6-4. The bond strength of brackets bonded to amalgam (see following discussion) is lower than that to etched enamel. In addition to forming a reliable bond, the ability of a resin to reduce or prevent demineralization (“white spot” caries) in the difficult-to-clean areas around orthodontic brackets and bands and to reduce damage to enamel during treatment are also important properties in this clinical scenario.

CRITICAL QUESTION

What are the materials and techniques needed to overcome the root canal system environment and create a hermetic seal with endodontic obturation systems?

Endodontic Sealers

Endodontic sealers are used in conjunction with a solid or semisolid core material to fill voids and seal root canals during **obturation**. These sealers, sometimes called *cements*, should fill and promote

a close seal between the core and the dentinal walls of the canal, preventing or minimizing leakage, entombing residual microorganisms, and preferably filling inaccessible areas of the root canal system. Sealer selection may influence the outcome of endodontic treatment. Historically, gutta-percha (a natural, malleable rubber related to latex) has been and continues to be used as the solid core material in combination with ZOE or calcium hydroxide cement, or an epoxy-based sealer. GIC and resin-modified GIC are also used as root canal sealers. These can chemically bond to root canal dentin but not to gutta-percha. There has been a surge of development in endodontic obturation materials to produce, via adhesive mechanisms, a sequence of bonded interfaces from dentin to sealer to the core obturation material and from the coronal to apical aspects of the canal space, including anastomoses, canal fins, cul-de-sacs, and isthmuses. These new developments will be discussed in Chapter 7, **Endodontic Sealers**.

The configuration of the root canal presents an unfavorable “C-factor” for these resin-based materials. C-factors can be extremely high, over 1000, for the canal configuration. Thus a resin endodontic sealer is subjected to severe polymerization shrinkage stresses during setting, which may cause debonding and gap formation along the periphery of the root canal obturation and adhesive interfaces. Gaps can form between the sealer and dentin wall or in between the solid core material (e.g., gutta-percha) and the sealer. Therefore root canal obturation inherently requires a number of different materials and involves multiple interfaces, thereby creating a greater challenge than most other applications of adhesive dentistry.

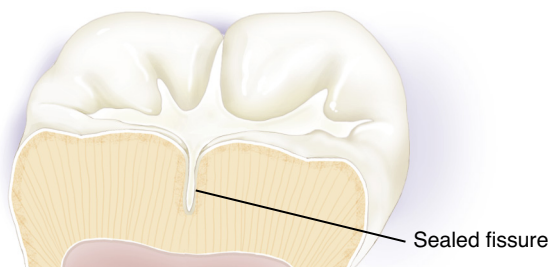
In a long, narrow space such as the root canal, the application of self-etching adhesives or any other bonding system becomes challenging and might not be uniform throughout the entire interface. Therefore, if resin infiltration into demineralized dentin and hybrid formation is not adequate to prevent movement of fluids inward through dentin, over time, the bond will be compromised, and the seal will fail. In addition, in bonding systems that contain volatile solvents, evaporation might be hindered. The canal anatomy is not only problematic to adhesive root canal obturation but also for the bonding of prefabricated posts.

A further problem is that some irrigating solutions (e.g., sodium hypochlorite, NaOCl) and intracanal medicaments can also have adverse effects on root canal dentin collagen and, consequently, on the longevity of endodontic bonding. In vitro studies have reported that NaOCl has deleterious effects on dentin collagen and is both concentration and time dependent. Destruction of the collagen matrix in mineralized tissues results in a less tough, more brittle substrate that might precipitate fatigue crack propagation during cyclic stresses. This might increase the susceptibility of the root-treated teeth to posttreatment crown or root fracture.

The results of a 2001 in vitro study indicate that root canals treated with 5% NaOCl have significantly lower bond strengths of C&B Metabond cement (Parkell, Inc., Edge-wood, NY) to dentin. However, it is important to note that the effects of endodontic irrigation on the bonding of resin cement to radicular dentin are dependent on the dentin-bonding system used.

CRITICAL QUESTION

How does amalgam bonding to dentin differ from composite bonding to dentin?



• **Figure 6-8** Schematic of a tooth cross section, illustrating penetration of a sealant into an occlusal fissure.

Amalgam Bonding

Mechanical retention and resistance forms continue to be used for amalgam restorations ([Chapter 8, Clinical Performance of Amalgam Restorations](#)). However, adhesive bonding methods for retaining and sealing amalgam restorations with dentin bonding to reduce microleakage and increase fracture resistance have also been investigated. Bonding agents employing M–R–X-type adhesive monomers such as 4-META (Parkell Inc., Edgewood, NY; [Figure 6-4](#)) have achieved some degree of success, but the mechanism for bonding amalgam to resin is predominantly mechanical. It is established during condensation of the amalgam into the viscous chemical-curing resin adhesive layer, producing macromechanical interlocking after polymerization. Thicker adhesive layers or interfaces have been shown to promote greater retention under certain conditions. For example, Amalgambond Plus with 4-META contains polymethylmethacrylate and forms a thick, viscous layer. Studies have shown that amalgam adhesive bond strength ranges from 6 to 15 MPa.

CRITICAL QUESTION

Can sealants prevent secondary caries progression when placed over underlying carious enamel or dentin?

Pit and Fissure Sealants

Various materials and techniques have been advocated for preventing caries in the susceptible pit and fissure areas of posterior teeth. The most widely used sealant techniques make use of resin systems that can penetrate into the pits and fissures and seal them against oral bacteria and acid demineralization. A cross section of a tooth with a pit and fissure sealant is shown schematically in [Figure 6-8](#).

Several types of resins, both filled and unfilled, have been employed as pit and fissure sealants. The commercially available products have been based on either the UDMA or *bis*-GMA monomers ([Figure 6-4](#)) that may be polymerized by either the

amine-benzoyl peroxide chemical activation–initiation system or by light activation, as discussed in [Chapter 5, Classification by Curing Method](#). The unfilled resins are available as colorless or tinted transparent materials. The filled resins are translucent and available either as tooth-colored or white materials.

The success of the sealant technique is highly dependent on obtaining and maintaining an intimate adaptation of the sealant to the tooth surface. Therefore the sealants must be of relatively low viscosity so that they will wet the tooth, flow, and penetrate the pits and fissures. To enhance wetting and mechanical retention of the sealant, the tooth surface is first conditioned by acid-etching, rinsed, and dried thoroughly, as described previously. The physical properties of the sealants are closer to those of unfilled direct resins than to those of resin-based composites.

The reduction in occlusal caries resulting from the careful use of pit and fissure sealants has been impressive. Consequently, the American Dental Association, the American Academy of Pediatric Dentistry, the American Society of Dentistry for Children, and the American Association of Public Health Dentistry have all endorsed the use of sealants as an effective therapy. Clinical studies have shown that the failure frequency of sealants is approximately 5% per year after a single application. In an early report, after 10 years, 78% of first permanent molars were free of caries after a single application of sealant, compared with only 31% of caries-free teeth in the unsealed matched pairs. Mertz-Fairhurst et al. found even more dramatic results in a study of sealed class I composite restorations where carious dentin was not removed. They showed that the lesions did not progress over a period of 10 years, as long as the sealants remained intact. Clinical trials in which sealants were intentionally placed in pits and fissures having caries have shown that as long as a sealant is well retained, no caries progression occurs.

If doubt exists about whether the pit or fissure is free from caries or not, it is still justified to place a sealant. If a dentist feels uncomfortable about sealing a potentially carious lesion and believes that a visual inspection of the potential lesion is required, another conservative approach can be taken that consists of minimal cavity preparation and the placement of an enamel–dentin bonded composite restoration combined with a sealant application. With such an approach, most of the occlusal surface is sealed. This restoration is called a *preventive-resin restoration* (PRR). The PRR treatment has exhibited a success rate of 75% after 9 years, a remarkably high success rate compared with traditional amalgam treatment.

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Buonocore MG: *The Use of Adhesives in Dentistry*, Springfield, IL, 1975, Charles C Thomas.

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Useful Websites

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7

Dental Cements

OUTLINE

History of Dental Cements

Indications for Dental Cements

Performance Criteria for Dental Cements

Solubility and Disintegration of Cements

Fluoride-Releasing Materials

Pulp Protection

Cements for Luting

Endodontic Sealers

Tri-/Dicalcium Silicate Cement

Calcium Phosphate Cements

Summary

KEY TERMS

Acid–base reaction Chemical reaction between a compound containing replaceable hydrogen ions (acid) and a substance containing replaceable hydroxide ions (base) that yields a salt and water; for aqueous liquid and powder cements, the liquid is the acid, and the powder is the base.

Atraumatic restorative treatment (ART) Clinical procedure performed without dental burs, air/water spray, or anesthesia that consists of manual excavation of cavitated carious tissues and restoration of the tooth cavity with a fluoride-releasing cement.

Bioactivity Reactive potential of a material to form a layer of hydroxyapatite-like material on its surface in vivo.

Calcium phosphate cements Cement that is used for bone regeneration that consists of powder (di-, tri-, or tetra-calcium phosphates) that is mixed with an aqueous solution from which hydroxyapatite precipitates.

Cavity liner Material to coat the bottom of a cavity preparation to protect the pulp; a liner is applied in a thin layer.

Cement Substance that hardens from a viscous state to a solid union between two surfaces; for dental applications, cements act as a base, liner, filling material, root canal sealer, or adhesive to bind devices and prostheses to tooth structure or to each other.

Cement base Material used to protect the pulp in a cavity preparation by providing thermal insulation and sometimes a medicament, usually thicker and more distant from the pulp than a cavity liner.

Cement thickness Distance between an abutment tooth and cemented prosthesis, influenced by the design of the prosthesis and the viscosity of the cement during seating.

Compomer A term derived from the terms *composite* and *ionomer*; a resin-based composite consisting of a silicate glass filler phase and a methacrylate-based matrix with carboxylic groups; also known as *polyacid-modified glass-ionomer cement*.

Endodontic sealer Material to prevent any transmittance of fluid or bacteria from the coronal to the apical region, used in conjunction with an obturation material such as gutta-percha.

Film thickness Thickness in μm of a cement 7 min after 150 N have been applied, which is the International Organization for

Standardization (ISO) and American Dental Association (ADA) method for determining the ability of a cement to spread under pressure.

Glass-ionomer cement (GIC) Cement that hardens following an acid–base reaction between fluoroaluminosilicate glass powders and an aqueous-based polyacrylic solution; also known as *polyalkenoate cement*.

Hydraulic cement Cement that requires water to cause the material to set.

Luting agent A viscous cement-like material that fills a gap between two surfaces to prevent dislodgement. The term *luting agent* originally referred to nonadhesive agents only but now also includes adhesive agents.

Maturation Process of aqueous cement strengthening after setting.

Mineral trioxide aggregate (MTA) A tri- and di-calcium silicate-based cement used for vital pulp therapy and other endodontic indications.

Pulp capping A procedure to treat pulp that has been exposed through caries removal or trauma, by the application of a medicament; *indirect pulp capping* is the term used when the pulpal exposure is incipient, such as when dentinal tubules are visible in the cavity.

Resin cement A resin-based composite material used for attaching fixed prostheses or orthodontic brackets; these cements are less viscous than resin composite restorative materials.

Resin-modified glass-ionomer cement (hybrid ionomer cement) Cement that combines a glass powder and an aqueous solution of polymerizable groups attached to the polyacrylic acid.

Varnish Material applied to the floor of a cavity; a solution of natural gum, synthetic resins, or resins dissolved in volatile solvent, such as acetone, ether, or chloroform; material applied superficially to a tooth to release fluoride.

Zinc oxide eugenol (ZOE) cement Cement based on the reaction between zinc oxide and eugenol.

Zinc phosphate cement Substance formed by the reaction between zinc oxide powder and phosphoric acid liquid that can be used either as a base or as a luting agent.

Naturally occurring waxes and resins have been used since time immemorial for covering the surface of broken teeth and adhering replacement materials, including bone, animal teeth, wood, and early naturally occurring polymers. However, problems arose with many “natural” materials exposed to the warm, moist, and often acidic oral environment, leading to their gradual failure in vivo. Modern dentistry has evolved to achieve improved clinical results, which include a wide variety of **cements** created by various chemical reactions. Cements are used for many indications and may be needed for short-term (days to weeks), intermediate-term (weeks to months), and long-term (years) retention of dental appliances (devices).

History of Dental Cements

In the 1800s, zinc oxide (ZnO) powder of good purity was found to react with eugenol at room temperature to form a functional cement. The ZnO–eugenol material was used as an impression material and temporary restoration and was eventually found to be obtundent with the pulp and suitable as a root canal sealer. Zinc oxide was observed to react with phosphoric acid to yield a material stronger than ZnO–eugenol, capable of securing gold alloy restorations to tooth preparations. The high acidity of the ZnO–phosphate cement was unsuitable for pulpal contact but a good insulator for use as a base. In the mid-20th century, ZnO was also used with carboxylic acid to produce a cement that was lower in acidity and capable of bonding to tooth structure.

When the zinc oxide in **zinc phosphate cement** was replaced with a glass powder, a semitranslucent esthetic filling called *silicate cement* was created. The longevity of the silicate cement restorations was unimpressive (<4 years) because the silicate cements have high solubility. Gradually, the silicate cements lost anatomical contour and degraded at the margins. Despite the deficiency, the occurrence of recurrent caries adjacent to these cements was rare. Laboratory studies showed that fluoride was released from the glass in silicate cements. The impressive anticariogenic potential of the silicate cements highlighted the ability of fluoride ions (F⁻) to inhibit demineralization.

The lessons learned from silicate cement and zinc carboxylate cement led to the development of **glass-ionomer cements (GICs)**, which contained a modified glass for the powder and polyacrylic acid for the liquid. Incorporating the polymerization technology of methacrylate resin into the liquid created dual-cured materials: acid–base and polymerization reactions. From this combination, **resin-modified glass-ionomer cement (RMGI)** evolved. Replacing the liquid component of RMGI with a water-free acidic polymerizable monomer created a light-curable single-component material called **compomer**, a term derived from the terms *composite* and *ionomer*. The goal of these two hybrid materials was to combine the strength of composite with the fluoride release and self-adhesion of glass ionomer in one material.

Around the mid-20th century, new attributes for dental cements were needed for use with gutta-percha points in endodontic therapy. These cements are denoted as endodontic sealers, which must cure in the moist root canal dentin. Furthermore, endodontic materials must ensure that oral bacteria cannot percolate through the root to the periapical bone; otherwise, serious infection persists or occurs. Esthetics are less important for endodontic cements than for supragingival indications. Several dental materials were adapted for endodontic use: **zinc oxide–eugenol (ZOE)**, polyvinyl siloxane, epoxy resins, and hydraulic ceramics (tri-/dicalcium silicate). In the 1990s, the **bioactivity** and sealing ability of tri-/dicalcium silicate cements became recognized and appreciated in dentistry.

This ceramic dental cement is now widely indicated for pulpal and periradicular contact, including endodontic indications.

Varnish has been used for pulpal protection, especially with amalgam in a cavity preparation. The use of varnish has declined with decreased amalgam use. However, surficial varnishes are popular, especially among pediatric dentists. These varnishes are placed on enamel to release fluoride to provide protection against caries and promote remineralization from acids in the oral cavity with calcium ions. Sealants based on resins are also used superficially on teeth to provide protection against caries.

In the 20th century, varnishes included silver ions, silver nitrate, and silver diammine fluoride solutions for arresting caries and reducing sensitivity. The hazard with silver compounds is imparting a black color to the caries, as discussed later.

Most current cements include polymers and ceramic powders. The remainder of this chapter is organized by general indications: pulp protection and enamel protection, fixed prosthodontic device cementation, endodontic restoratives, and sealing.

Indications for Dental Cements

Dental cements are classified according to their major component, as shown in **Table 7-1**, which includes their general indications. Several formats are offered for dental cements: powder and liquid, two pastes, or single component. Biocompatibility, durability for the indication, and safety for the patient and dental practitioner are important general cement attributes, all with a “reasonable” price. Some cements achieve their biocompatibility by being mildly cytotoxic, whereas others are bioinert or bioactive, as described later. The biocompatibility of dental cements is discussed in general terms in this chapter. Principles of biocompatibility are discussed in **Chapter 17, Biocompatibility**.

Other characteristics are designed for a cement’s unique indications, such as viscosity. For pulpal protection or surficial tooth sealing, a fluid layer is usually suitable. A medium-viscosity cement is used for **cavity liner** or cement-base indications. For adhering an appliance, a cement must have a sufficiently low viscosity to flow along the interfaces between the tooth tissue and a restorative. A low-viscosity cement is also needed to enable an endodontic sealer to fill complex root canal anatomy. Orthodontic bands require a low-viscosity cement, but orthodontic brackets require higher-viscosity cements to keep orthodontic brackets from drifting before the cement is cured. Base/liner materials should flow and set within, but not out of, the cavity preparation. Viscous cements are used for filling perforations, for root-end filling, or for covering pulps after a pulpotomy. Whether low or high viscosity, a low-contact-angle material is useful for wetting the surface of enamel or dentin or a prosthetic device.

Cements must harden (set) within a reasonable time that depends on the indication, ranging from minutes to days. Strength requirements vary from a compressive strength of 35 MPa for **pulp capping** and base materials to 50 MPa for aqueous cements for the adhesion of devices. The strength should be appropriate for the indication and increase during **maturation**. For instance, the tri-/dicalcium silicate cements mature over about 1 month. All cements undergo a chemical reaction in vivo. Varnishes set by evaporation of the solvent to form a coherent protective layer. Two-part cements begin setting/hardening when the components are mixed. Single-component polymer-based cements set through polymerization activated by visible light. Dual-cured **resin cements** use both chemical and light-curing mechanisms to maximize polymerization. The hydraulic bioactive cements set by

TABLE 7-1 Overview of Dental Cements

Powder/Liquid Systems Materials	Powder	Liquid	Reaction Type	Indications
Zinc phosphate	Zinc oxide and magnesium oxide	Phosphoric acid, water	Acid–base reaction	Cementing metallic fixed prostheses
Zinc oxide–eugenol	Zinc oxide	Eugenol	Acid–base reaction	Pulp protection, temporary cement
Zinc oxide–eugenol (EBA modified)	Zinc oxide	Eugenol, EBA	Acid–base reaction	Pulp protection, temporary cement
Zinc polycarboxylate	Zinc oxide and magnesium oxide	Polyacrylic acid, water	Acid–base reaction	Metallic fixed prostheses short spans or crowns
Glass ionomer	Fluoroaluminosilicate glass	Polyacrylic acid, polybasic carboxylic acid, water	Acid–base reaction	Cementing crowns (alumina, zirconia metal), metal posts and core restoration
Resin-modified glass ionomer (hybrid ionomer)	Fluoroaluminosilicate glass, chemical- and/or light-activated initiator(s)	Polyacrylic acid, water-soluble methacrylate monomer, water, activator	Light- or chemical-activated polymerization and acid–base reaction	Metal, lithium disilicate, alumina or zirconia prostheses,* metal posts/core
	Fluoroaluminosilicate glass, metallic oxides, sodium fluoride, chemical- and/or light-activated initiator(s)	Dimethacrylate/carboxylic monomers, multiple functional acrylate monomers, water, activator for chemical activation	Polymerization by light- and chemical-activation and acid–base reaction	
	Fluoroaluminosilicate glass, nonreactive filler, reactive monomers	Nonreactive filler, methacrylate-modified polyalkanoic acid, water-soluble methacrylate monomer, water	Light-activated polymerization and acid–base reaction	
Epoxy	Methenamine, titania, silver	Bisphenol A, epichlorohydrin resin	Chemical crosslinking polymerization of epoxide	Root canal sealing
Tri-/dicalcium silicate	Tri-/dicalcium silicate and radiopaque powder	Water-based liquid	Hydration with liquid	Pulpal protection, periradicular contact, endodontic sealing
Two-Paste Systems Materials	Base Paste	Catalyst Paste	Reaction Type	Indications
Compomer	Fluoroaluminosilicate glass, metallic oxides, sodium fluoride, chemical- and/or light-activated initiator(s)	Dimethacrylate/carboxylic monomers, multiple functional acrylate monomers water, activator (for chemical cure)	Light or chemical activation of polymerization and acid–base reaction	Cavities in deciduous teeth, cervical cavities in adults, anterior proximal restorations in adults, small load-bearing restorations in adults, temporary
Resin cement	Methacrylate monomers, fillers, light-activated initiator(s)	Methacrylate monomers, fillers, activator (for chemical cure)	Polymerization by light and chemical activation, or chemical activation only	Ceramic veneers, Maryland bridges, lithium disilicate, alumina, zirconia, cores and posts
	Polymethyl methacrylate polymer beads	Liquid 1: Methacrylate monomers Liquid 2: Catalyst	Chemical-activated polymerization	
Disilicylate	Butyl ethylene glycol salicylate resin, bismuth oxide	Resimpol natural resin, 13% “MTA” (tri-/dicalcium silicate and tricalcium aluminate?), titania and silica	Chemical-activated polymerization	Endodontic sealing
Disilicylate	Glycol disilicylate, titanium dioxide and barium sulfate, titania, zinc oxide	Ethyl toluene sulfonamide, calcium hydroxide, zinc oxide, zinc stearate	Chemical-activated polymerization	Pulp capping
Epoxy	Bisphenol-A epoxy resin, bisphenol-F epoxy resin, calcium tungstate, zirconium oxide, silica, iron-oxide pigments	Dibenzylamine, aminoadamantane, tricyclodecane-diamine, calcium tungstate, zirconium oxide, silica, silicone oil	Chemical-activated polymerization	Endodontic sealing

TABLE 7-1 Overview of Dental Cements—cont'd

Single Component Materials	Paste or Liquid	Reaction Type	Indications
Compomer	Methacrylate monomer, acidic monomer, fluoroaluminosilicate glass, initiator	Light-activated polymerization	Cavities in deciduous teeth, cervical cavities in adults, anterior proximal restorations in adults, small load-bearing restorations in adults, temporary
Varnish	Resins, organic solvent (acetone); chloroform ether may include silver, fluoride, or calcium compounds	Evaporation of solvent	Pulp protection, surficial ion release for caries prevention or remineralization
Inert	Methacrylate monomers, initiator, ceramic fillers	Light-activated polymerization	Cementing ceramic restorations or orthodontic brackets
Tri-/dicalcium silicate	Methacrylate monomers, initiators, tri-/dicalcium silicate, barium zirconate	Light-activated polymerization	Pulp-capping, pulpotomies
Tri-/dicalcium silicate	Organic liquid, tri-/dicalcium silicate, radiopaque powder	Hydration in vivo	Pulpotomies, endodontic sealing
Calcium hydroxide	Iodoform, silicone, calcium hydroxide	Nonsetting	Primary tooth pulpectomy
Tri-/dicalcium silicate	Tricalcium silicate, salicylate resin, titanium oxide, calcium tungstate	Nonsetting	Primary tooth pulpectomy

EBA, ethoxybenzoic acid.

*Don't use for anterior because of opacity.

reaction with water that is either included in two-part systems or absorbed from the tooth. The exception is the nonsetting materials used with primary teeth after a pulpectomy, where a cement should not interfere with exfoliation.

Long-term retention of devices is important for crowns and bridges. However, temporary cements are sometimes needed, for instance, when transient devices are placed during prosthetic treatments. Dental cements are crucial for orthodontic brackets and bands, but the durability of these materials can be less than other cements because orthodontic treatments usually last about 2 years. Sealants and cements to reduce sensitivity (by occluding exposed dentinal tubules) are not expected to last long term.

Performance Criteria for Dental Cements

Dental cements must solidify into a biocompatible mass in the oral cavity and function over time in vivo by resisting hydrolysis (degradation by water). Properties of dental cements vary, but those that are often compared include the mixing time, working time, setting time, **film thickness**, compressive strength, and vulnerability to acid. Requirements for dental cements (base/liner and luting materials) have been codified in International Organization for Standardization (ISO) Standards 9917-1 and 9917-2 (Dentistry—Water-Based Cements) and ISO 6876:2012 (Root Canal Sealing Materials), where the test methods for these properties are described. These standards apply to water-based luting cement, bases, linings, restorations, core buildup materials, and root canal sealing. See [Table 7-2](#) for the requirements. Except

for root canal sealers, cements should set in less than 8 minutes (min) and resist acid erosion.

Solubility and Disintegration of Cements

Cements are often placed supragingivally and exposed to a variety of acids produced by microorganisms or as components of foods and drinks. ISO 9917-1 describes the erosion test of impinging a 0.1-M solution of lactic acid/sodium lactate (pH = 2.74) on water-based cements. The depth of erosion after 24 hours (h) is measured as mm/h. The results show that the rate of erosion decreased from conventional GIC to hybrid GIC to compomer. The solubility procedure described in ISO 4049 for dental composites uses the weight (mg) and volume (mm³) of the specimen before immersion in water and the weight of the specimen after 5 days of immersion, and then desiccation. The solubility is calculated by dividing the weight changes by the volume. ISO 6876 for endodontic sealers measures the weight of the specimen before 24 h of immersion in water, and the weight percentage of residue is reported.

Testing conditions have been shown to significantly influence the solubility, such as varying the pH, the electrolytic concentration of the storage media, the soaking or impingement of a test medium on the cement, the powder-to-liquid (P/L) ratio of the cement, and the testing duration. For example, lowering the pH and P/L ratio will generally increase solubility. Delaying exposure to a storage medium decreases solubility. Some cements show no solubility (by weight) when concurrent dissolution and water sorption occur. Therefore poor correlation has been found

TABLE 7-2 ISO Requirements

ISO 9917-1 Water-Based Cements—Part 1: Powder/Liquid Acid-Base Cements

Cement Type	Zn PHOSPHATE		Zn POLYCARBOXYLATE		GLASS IONOMER	
	Luting	Liner or Base	Luting	Liner or Base	Luting	Liner or Base
Maximum mixing time (min)	2.5	2	2.5	2	1.5	1.5
Final setting time (min)	8	6	8	6	8	6
Maximum film thickness (μm)	25	nr	25	nr	25	nr
Minimum compressive strength (MPa)	50					
Maximum acid erosion (mm)	0.3		0.4		0.17	

ISO 9917-2 Water-Based Cements—Part 2: Resin-Modified Cements

Cement Use	Luting	Liner or Base	Restorative
Minimum working time (min)	1.5	1.5	1.5
Minimum setting time (min)	8	6	6
Maximum film thickness (μm)	25	nr	
Minimum flexural strength (MPa)	10	10	25

ISO 6876 Root Canal Sealing Materials/ADA 57 Endodontic Sealing Materials

Property	Requirement
Flow (mm)	>17
Working time	To be stated by manufacturer in minutes or hours
Setting time	To be stated by manufacturer in minutes or hours
Maximum film thickness (μm)	50
Solubility (%)	<3
Radiopacity (mm of equivalent Al)	>3
Dimensional stability (ADA 57 only)	<0.1% expansion, less than 1% shrinkage

ADA, American Dental Association; nr, no requirement.

for solubility data from the acidic-erosion and passive-weight-loss tests. In vitro data show that cement solubility differs among categories of materials and products. For the cements that rely on water to set, the solubility increases from glass ionomer to zinc phosphate and polycarboxylate cements. The solubilities between zinc polycarboxylate cement and zinc phosphate cement were not significantly different when mixed as recommended. However, a reduction in the powder-to-liquid ratio for zinc polycarboxylate reduced the viscosity and produced a cement that disintegrated rapidly. Zinc phosphate cements have a relatively low solubility in water; however, in vivo disintegration occurs with the lactic, acetic, and citric acids present in foods.

With solubility being inversely proportional to the resin content, resin cements are the least soluble of all dental cements, especially hydrophobic resins. The low solubility of resin cement makes this material suitable for cementing all-ceramic or resin-based restorations, where more cement may be exposed compared with metal or metal-ceramic restorations. Polymerizing monomers in glass-ionomer cements (RMGIs) have reduced the solubility compared with GIC.

The durability of some cements has been tested by placing small specimens of the cements in intraoral appliances that can

be removed from the mouth to measure the loss of material. In one study, cements were inserted in tiny wells placed in the proximal surfaces of cast crown restorations. These crowns were cemented with temporary ZOE cement. After 1 year, the crowns were removed, and the cement loss was measured. GIC degraded the least, followed by zinc polycarboxylate cement, zinc phosphate cement, and zinc polycarboxylate cement mixed in a lower P/L ratio.

The solubilities of endodontic sealers based on ZOE and early formulations of glass ionomer were near the maximum allowed in ISO specifications (3%). ZOE-based root canal sealers have been used successfully for decades in endodontics, despite their high solubility. Sealers with epoxy or polyvinyl siloxane (PVS) bases have significantly lower solubility among endodontic sealers. The tri-/dicalcium silicate cements do not meet this limit after 24 hours; however, after longer times, these materials become less soluble. Immediately after setting, the tri-/dicalcium silicates have calcium hydroxide on the surface, which is beneficial for bioactivity but appears as solubility. Nevertheless, the tricalcium silicate sealers are highly successful clinically.

The variety of dental cements encompasses many material categories, and the properties vary widely, as discussed herein.

Fluoride-Releasing Materials

The anticariogenic potential of silicate cement confirms the ability of F^- to inhibit demineralization and lead to the development of several fluoride-containing restorative materials and cements: conventional glass ionomers, resin-modified glass ionomers, polyacid-modified composites (compomers), and fluoridated varnishes. For the fluorosilicate glass-based materials, fluoride is first dissolved in the matrix from the glass during the **acid–base reaction**, and then released to the oral cavity. For fluoridated varnishes, the fillers incorporated in the material dissolve partially upon contact with saliva, and then F^- is released from the varnishes. The rate of fluoride release depends on the cement matrix, porosity, and nature of the fluoridated filler (i.e., type, amount, particle, and size). **Figure 7-1** illustrates the typical behavior of fluoride release from dental materials.

In vitro data have shown that fluoride release from GIC remains detectable for years, although the rate of release is reduced by a factor of 10 within the first few months (**Figure 7-1, A**). The release rate and duration depend on the cement matrix; porosity; and the fluoridated filler's type, amount, silanation, and particle size. **Figure 7-1, B & C** illustrate the typical behavior of fluoride release from dental materials.

Factors Affecting Fluoride Release in Vitro

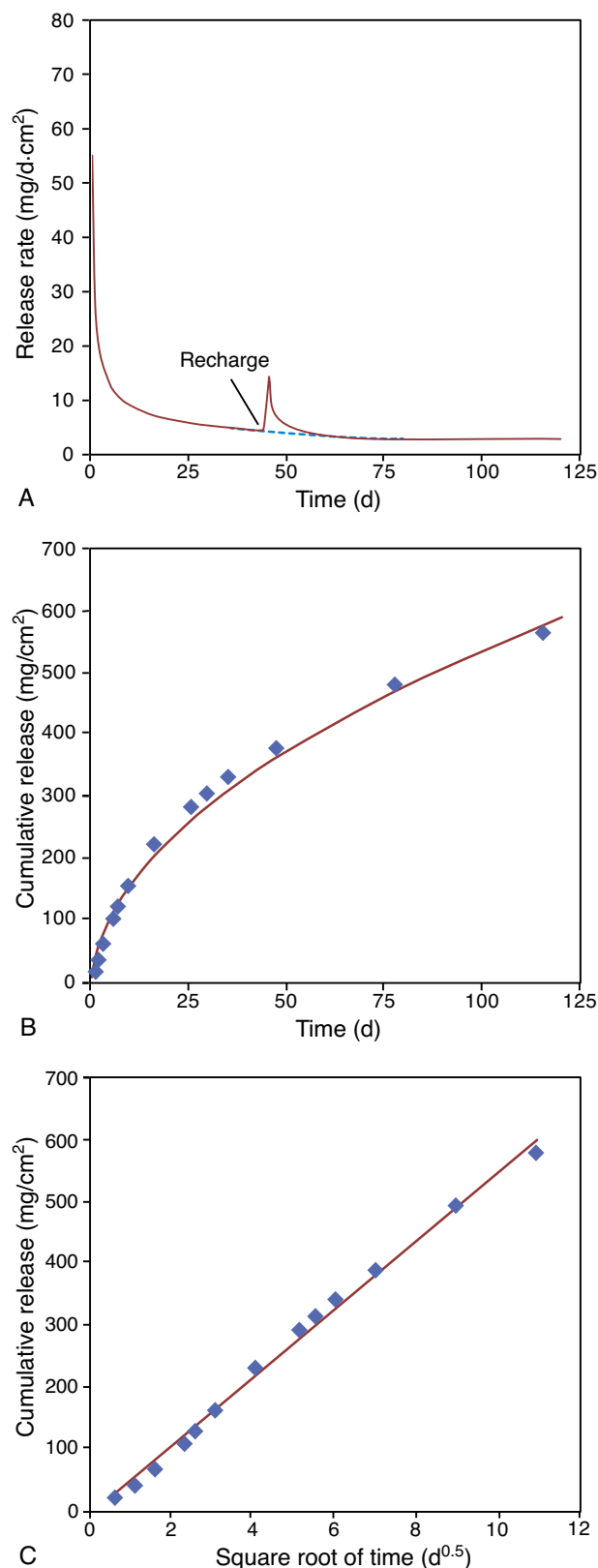
Fluoride-release studies usually are conducted in vitro, where the experimental conditions are controlled and the fluoride release is easier to measure. Also, the intrinsic characteristics of the material—such as formulas, filler compositions, ratios of component mixing, mixing procedure, and curing time—can be studied more easily. For such in vitro tests, the protocols have varied in terms of the composition and pH of storage media, the frequency of the storage solution change, and plaque and pellicle formation.

When the demineralization–remineralization cycling is used in in vitro studies, higher fluoride release is observed in acids. However, ion-enriched (ions other than F^-) storage media, such as artificial saliva, reduce the release of fluoride and surface coatings from human saliva. The presence of esterase or hydrolases in the storage media or on the surface of the material increases fluoride release. Although removal of the outer layer of the material by air polishing or finishing can lead to higher release, toothbrushing has not been found to affect fluoride release.

Clinical Significance

In vitro studies have shown that fluoride-releasing restoratives inhibit the enamel and dentin demineralization produced by acidic gels or demineralizing buffer solutions. The inhibition of enamel demineralization reached up to 7 mm from the edge of the material. These results were confirmed by microradiographic assessments of the lesion depth of artificial caries and the mineral density of enamel adjacent to a conventional and a resin-modified glass-ionomer. For both materials, lesion depth increased, and mineral density decreased, with increasing distance (1 to 3 mm) from the restoration margin.

Fluoride release varies between categories of material and brands and is influenced by the material and the material's setting mechanisms, the fluoride content, and the testing conditions. Clinical studies have not clearly shown whether the initial burst or long-term release of F^- ions is clinically more important to prevent caries. Despite the proven effects from in vitro studies, clinical studies



• **Figure 7-1** Typical fluoride-release profiles. **A**, Release rate versus time; the spike reflects fluoride recharging, and the blue dotted line represents the fluoride release where no recharging has occurred. **B**, Cumulative release over time; the diamonds are experimental data of **(A)** without recharging, and the curve is the best-fit curve of Y (total release) = $a + b \cdot (\text{time})^{1/2}$. **C**, The same data in **(B)** plotted against the square root of time, revealing a linear relationship. The effect of recharging is not shown in **(B)** or **(C)**.

conflict as to whether these materials sufficiently prevent or inhibit recurrent caries compared with nonfluoridated restoratives. Further clinical studies, preferably in split-mouth designs, are needed to evaluate the impact of fluoride-releasing restoratives on recurrent caries development and progression, especially in patient groups that have limited access to or low compliance with prophylactic measures.

An in situ study compared the effectiveness of a conventional GIC, an RMGI, a compomer, and a fluoridated composite for resistance to enamel lesion formation using intraoral appliances embedded with these materials. Intraoral appliances were worn by the subjects for 4 weeks without additional application of topical fluorides. The results showed that only one ion-releasing material led to significantly lower lesion depth and mineral loss. No other materials had a preventive effect on recurrent caries. Clinical studies of fluoride-releasing composites often show no differences in the occurrence of recurrent caries.

Fluoride Recharge

Dental restoratives are frequently exposed to exogenous sources of fluoride, such as fluoridated dentifrices, mouth rinses, fluoride gels, and varnishes. These released fluoride ions can be absorbed by the dental restoratives to “recharge” with fluoride. A common recharging method is exposing the restorative to a concentrated fluoride agent such as 0.02% NaF solution (90 ppm) or 1.23% (12,300 ppm) acidulated phosphate fluoride (APF) solution for 4 to 5 min, although treatments up to 1 hour have been reported. Recharging is more effective with acidic fluoridating agents, such as APF. However, APF is known to cause surface damage of some restorative materials. The ability of a restorative material to be recharged and serve as a fluoride reservoir depends on the type and permeability of the material, the frequency of fluoride exposure, and the concentration of the fluoridating agent. Glass ionomers, resin-modified glass ionomers, and compomers are recharged more easily than composite resin-based materials. In vivo fluoride recharging is influenced by saliva and plaque. The higher viscosity of saliva reduces the diffusion of ions in and out of the material. The formation of a surface pellicle is a barrier hampering the recharging process. The release data for recharged materials is significantly higher in the first 24 hours but decreases within several days to the preexposure level (Figure 7-1, A), suggesting that the initial release may occur partly by washout of fluoride ions retained on the surface or in the pores of the material. The level of release after recharging depends on the concentration of the recharging medium and the duration of treatment.

CRITICAL QUESTION

What is the benefit of calcium hydroxide in contact with pulpal tissue?

Pulp Protection

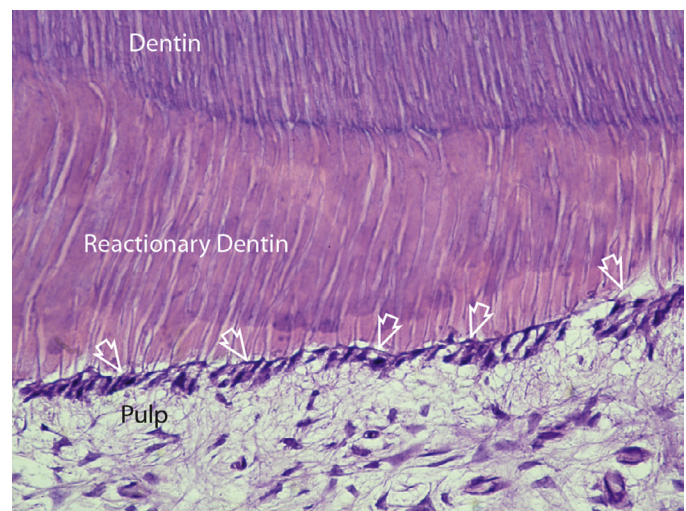
Tooth enamel is a translucent crystalline bioceramic but is vulnerable to acids and the repeated stress of a lifetime of chewing. The underlying dentin may be exposed to the oral cavity when the enamel is worn, chemically eroded by acidic foods or cariogenic bacteria, mechanically abraded by food or opposing teeth, fractured, or prepared for restoration. Depending on the remaining dentin thickness, the exposed dentinal tubules provide a communication path to the pulp for acids and microbiological insults. The dentin must be covered to minimize further damage. When

metallic material is used to restore the tooth, discomfort may arise from hot or cold nutrition or galvanic contact with metal restoratives on opposing dentition. During restorative procedures, the acidic components of some dental cements may irritate the pulp before setting. Therefore pulp protectants are required when little protective dentin is left after a cavity preparation.

Pulp protectants for cavity preparations approximating the pulp are denoted as *pulp-capping materials*, *varnishes*, *cavity liners*, or *base materials*. Pulp-capping materials are in direct contact with the pulp, and their biocompatibility is crucial to the pulp's healing. Varnishes as very thin resin layers used to plug and block the dentinal tubules exposed in a cavity preparation. Cavity liners are thin layers and are used for indirect pulp capping when the remaining dentin is less than 1 mm and are more protective than varnishes. Base materials are placed in thicker layers than liners and are commonly placed farther from the pulp. The base material is needed for insulation from the thermal, chemical, or galvanic irritations that may occur with restorative materials.

Pulp-Capping Materials

Pulp-capping agents are used when the pulp has been exposed and bleeding is frank. The best pulp-capping and cavity-liner materials are bioactive and antimicrobial. *Bioactivity*, as defined in ISO 22317, is the spontaneous formation of a thin layer rich in Ca and P, similar to hydroxyapatite, on the surface of a material in vivo or synthetic body fluid. Bioactivity occurs by the release of calcium and hydroxide ions that create a high pH (alkaline), thus causing the precipitation of calcium phosphate from the supersaturated body fluids in the vicinity of their surface. Bone morphogenic protein (BMP) and transforming growth factor-beta one (TGF- β 1) may be solubilized from the bone or dentine by the high pH and released to stimulate repair. The pulp can heal by forming pulpal odontoblasts on the calcium phosphate layer of the bioactive materials, forming reparative dentin. Such a histological result is shown in Figure 7-2. Bioactive pulp-capping



• **Figure 7-2** Reactionary dentin. Histological section of a human tooth submitted to a slight pathological stimulus from a deep cavity filled with light-cured glass-ionomer cement, and then extracted 30 days after the procedure. The remaining dentin thickness is 287 μ m at the thinnest region. Note that the pulp tissue subjacent to the continuous odontoblast layer (hollow arrows) does not show inflammation. (Courtesy Dr. Carlos Alberto de Souza Costa.)

agents include calcium hydroxide powder and tri-/dicalcium silicate materials.

Calcium Hydroxide

Calcium hydroxide medicaments are available as powder, one-paste, or two-paste products with radiopaque fillers. Calcium hydroxide powder may simply be mixed with water and placed, or some products disperse the powder in a carrier such as polyethylene glycol liquid, such as UltraCal (Ultradent Inc.). Other products may include calcium hydroxide in a resin formula that sets chemically or with light, such as Dycal (Caulk Dentsply Sirona). Calcium hydroxide is sparingly soluble in water and does not set into a hardened cement during the procedure but gradually converts to calcium carbonate by carbon dioxide in the blood and oral fluids over time. Such products must not be left on the margins of the cavity preparation; otherwise, the margin will not be properly sealed. Calcium hydroxide is beneficial because of a high pH, which makes this material antimicrobial. However, calcium hydroxide alone does not set or provide much thermal insulation but is bioinert. Histologically, calcium hydroxide stimulates reparative dentin when placed on the pulp, although the reparative dentin may have tunnel defects.

CRITICAL QUESTION

Why is MTA cement biocompatible and considered bioactive?

Tri-/Dicalcium Silicate

Tri-/dicalcium silicate (tricalcium silicate, for short) products are also known by the names **mineral trioxide aggregate (MTA)**, *calcium silicate*, *biosilicates*, or *bioceramics*. Chemically, the predominant compounds in these cements are tricalcium silicate and dicalcium silicate powders with inert radiopaque ceramic powders. The tricalcium silicate powders are unique ceramic compounds because they set with water and form calcium hydroxide as a reaction product within a hard matrix of hydrated tri- and dicalcium silicate. The calcium hydroxide reaction product renders bioactivity and imparts antimicrobial properties. Furthermore, because the calcium hydroxide is within a matrix, the alkalinity is sustained longer than in calcium hydroxide alone. This type of cement is thermally insulating and seals very well, without shrinkage.

For pulpotomies, hemorrhage should be controlled with a cotton pellet moistened with saline, a dilute solution of sodium hypochlorite (0.5% to 1.0%) before placement, to avoid blood seeping into the cement and ensure removal of enough affected pulp. The consistency of the tricalcium silicate can be fluid or putty-like for pulpal placement. After placement, any restorative material, including ZOE, GIC, hybrid ionomer liner, or flowable compomer or composite, can be placed immediately over the tricalcium silicate without waiting for a full set of tricalcium silicates. Bonding agents do not adhere to tricalcium silicates, and etching should not be performed directly on tricalcium silicates. The precipitation of hydroxyapatite at interfaces with the tissue should prevent the tricalcium silicates from being dislodged. After pulpotomy treatment, the pulp should be periodically assessed for vitality, as an indication of a dentinal barrier forming beneath the tricalcium silicate cement. Tricalcium silicates have been added to the resin matrix as pulp protectant, such as TheraCal and TheraCal PT (Bisco). These products set by light curing or dual curing of the resin, but their bioactivity is lessened by the resin encapsulation of the bioactive component.

The properties and applications of tri-/dicalcium silicate will be discussed in more detail later in the chapter.

Formocresol and Ferric Sulfate

Formocresol and ferric sulfate have been used as protective medicaments for partial or complete pulpotomy procedures, among other techniques, including electrosurgery and laser cautery. Ferric sulfate and formocresol staunch the bleeding pulp, but neither material is bioactive. By far, formocresol has been the most popular among pediatric dentists. Ferric sulfate-treated pulpotomies have led to the unfortunate consequence of root resorption. Calcium hydroxide has not been popular in pediatric dentistry because this material has been less successful with pulpal inflammation and tooth resorption in small, thin primary teeth. The bioactive tricalcium silicate-based products are superseding the use of formocresol or ferric sulfate medicaments for pediatric pulpotomies, with a better success rate for retention before exfoliation.

Pediatric pulpotomies may fail or may not be suitable because of deeper infection of the pulp. For these cases, the pulp is extirpated, and the canal is filled with a nonsetting medicament. The filling material is nonsetting to avoid interference with the primary tooth's exfoliation. These materials should be radiopaque. Two such materials contain calcium hydroxide in silicone oil or tricalcium silicate powder in salicylate resin.

CRITICAL QUESTION

What is the purpose of using cavity varnishes, and why is copal varnish no longer used as often as it was during the 1960s through 1990?

Cavity Varnishes and Liners

When the remaining dentin thickness is less than 1 mm, irritants must be prevented from reaching the pulp through the dentinal tubules by placing a protective layer. The classic pulp protectant is a cavity varnish, which prevents pulpal irritation by occluding the exposed dentinal tubules.

Varnishes are solutions of synthetic resins or natural gums, such as copal or rosins, in an organic solvent (ethanol, acetone, chloroform, or ether). The varnish is applied as a thin coating on the dentin, which forms a coherent layer as the solvent evaporates in about 30 seconds. At least two layers of varnish should be applied to obtain a complete, continuous coating with few pinholes. Each varnish layer should be thoroughly dried before proceeding. Varnishes are applied with a disposable brush or a small pledget of cotton. For infection control, a used varnish applicator should not be inserted in a varnish bottle; hence, unit-dose containers are common.

Additional cavity-liner products include low-viscosity ZOE, glass ionomer, calcium hydroxide products, and the tricalcium silicates. Calcium hydroxide-containing products are preferred for cavity lining, for the same reason as the pulp-capping materials: bioactivity. Some liners adhere to the tooth, enhancing their ability to seal the dentinal tubules. Glass ionomers are less desirable in the vicinity of the pulp because of their acidity, but resin-modified glass ionomers are used. Varnish is not indicated or needed when adhesive materials are selected for restorations. The resin bonding systems serve the same role as varnish.

Fluoridated Varnishes

Varnishes containing fluoride are applied superficially on teeth. Varnishes reduce sensitivity by occluding dentinal tubules and

provide fluoride release. Typically, these varnishes contain 5% sodium fluoride to elute fluoride ions, although others contain calcium fluoride or amorphous calcium phosphate. Varnish films are temporarily effective but must be reapplied for caries prevention at hygiene appointments. Superficial varnishes are often flavored for patient acceptance (Figure 7-3, left).

Silver nitrate has a long history of use to arrest caries. Later, a Japanese researcher developed a 38% silver diammine fluoride solution for arresting caries and reducing dentinal sensitivity (Figure 7-3, right). The silver ions are dissolved in an ammonia solution, which can attack and kill bacteria. The term *silver diammine fluoride* (SDF) has been accepted in dentistry for $\text{AgF} \cdot (\text{NH}_3)_2$. SDF solutions contain twice the fluoride present in a 5% NaF varnish. This solution will arrest caries by precipitating the silver ions but will darken carious lesions with silver precipitates. Darkening of the tooth can be alleviated by using a potassium iodide solution after application of the SDF. This material is convenient to use for the medically compromised or bedridden and primary teeth, despite the discoloration.

Cement Bases

Cement bases are more distant from the pulp and placed at the bottom of cavity preparations. Bases provide thermal or galvanic insulation (Chapter 3, [Clinical Significance of Galvanic Currents](#)), although eliminating communication to the pulp is also important. Being farther from the pulp allows some acidic materials to be used, such as zinc phosphate cement. Zinc phosphate cement has been an effective base material because this cement is thermally insulating but has a low pH (acidity) and therefore requires another material under the cement to protect the pulp.



• **Figure 7-3** Flavored fluoride varnish for surface application to teeth, especially primary teeth (left), and silver diammine fluoride solution cleared in the United States for sensitivity treatments, used off-label for caries treatment (right). (Courtesy Elevate Oral Care.)

When mixed as a base, zinc phosphate cement should be kept cool and mixed to a thick, nontacky, putty-like consistency that slows the reaction and minimizes free acid on the surface when placed.

ZOE, zinc polycarboxylate, fast-setting glass ionomers, calcium hydroxide, and tricalcium silicate cements have been used as cavity bases. All these cements contain ceramic powders, which inherently have lower thermal and electrical conductivity than metals (Table 7-3). Heat transfer is a complex phenomenon that depends on the material's heat capacity, thickness, and density (Chapter 3, [Thermal Properties](#)).

Cement bases should be strong enough to withstand condensation forces during placement of restorative materials, especially amalgam, and the forces during mastication or bruxing. Table 7-4 shows the compressive strength of representative dental cements over 24 hours. For most dental cements, the strength increases rapidly over 30 min and keeps increasing on the first day. Notably, the tricalcium silicate cements mature by hydration more slowly and gain their strength over 1 month, but especially during the first week. The minimum strength required of base materials to resist masticatory forces has not been determined because of the complexity and the influence of the design of the prepared tooth cavity. However, a study of amalgam restorations placed over a

TABLE 7-3 Thermal Conductivity of Cement Base and Reference Materials

Material	Approximate Thermal Conductivity (mcal/cm-s-K)
Dentin	1–2.3
Enamel	1.6–2.2
Tricalcium silicate cement	0.7
Glass	2–2.5
Zinc phosphate cement	2.5–3.1
Zinc oxide–eugenol	4.0
Amalgam	5.4
Stainless steel	38
Gold	740

TABLE 7-4 Compressive Strength of Cement Base Materials

Material	7 Min (MPa)	30 Min (MPa)	24 Hours (MPa)
Zinc oxide–eugenol	2.8	3.5	5.2
	6.2	6.9	12.4
	15.9	20.7	24.1
Calcium hydroxide	3.8	4.8	10.3
	7.6	6.2	8.3
Tricalcium silicate	~0	Not determined	14–40
Zinc phosphate	6.9	86.9	119.3

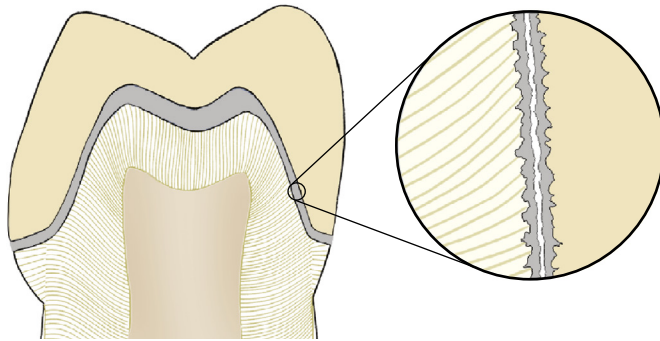
hard-setting calcium hydroxide base showed no evidence of failure, even though the strength of the material was only about 10 MPa after 1 day. For a class I tooth preparation where the base is supported on all sides by tooth structure, less strength is necessary than is required for class II preparations.

CRITICAL QUESTION

During the initial seating of a three-unit fixed partial denture (bridge), the prosthesis fits the prepared tooth perfectly and appears to be retained on the tooth so tenaciously that removal requires a great deal of force. Why is cement required for retention under this condition?

Cements for Luting

The first zinc oxide–based cement for cementing fixed prostheses was not adhesive to the tooth or metal prostheses. The cement functioned by filling the microscopic space between the device and the tooth and hardening to a high cohesive mass, which prevented dislodgement (Figure 7-4). The mechanical retention is



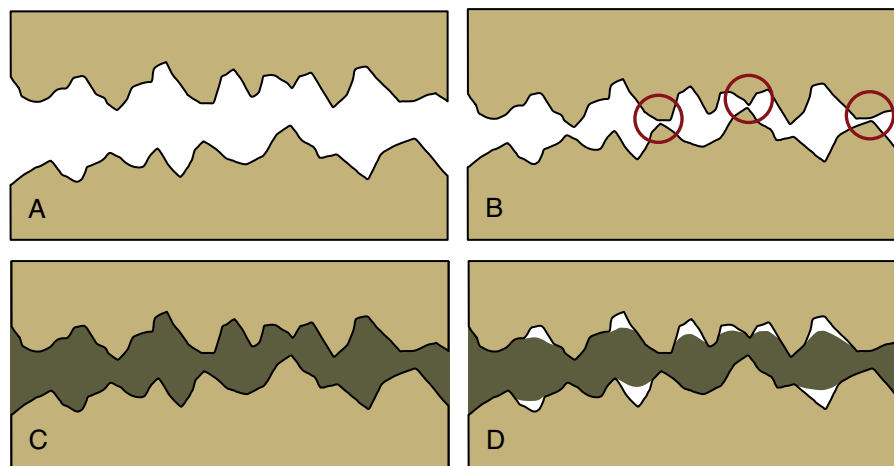
• **Figure 7-4** Diagram of the suggested mechanism through which a dental cement provides mechanical retention of a gold crown. The cement penetrates irregularities in the tooth structure and the casting. Upon hardening, these retentive sites aid in retaining the cast crown in place. The enlargement shows a fracture through the cement, resulting in dislodgment of the crown.

obtained by the combination of the microscopically rough tooth and prosthesis surfaces, along with the rigid cement that fills the gaps. This mechanical retention is referred to as *luting*, where zinc phosphate is the dominating cement. The degree of cement retentiveness for a given restoration relies on many factors: prepared tooth form, height, number of abutments, accuracy of superstructure fit, distribution of the cement, and occlusion. Dental prostheses that are mechanically retained include the following: (1) fixed prosthodontics made of metal, ceramic-veneered metal, or ceramic; (2) temporary restorations; (3) pins and posts used for retention of restorations; and (4) implant superstructures. As discussed in Chapter 6, *Luting Agents*, *luting* traditionally refers to the use of nonadhesive materials for retaining prostheses, and *bonding* refers to the use of adhesive bonding materials. The distinction has faded in the literature; the use of adhesive bonding medium is also referred to as *luting*.

When a device is seated without a *luting agent*, point contacts are made between the tooth and the appliance (Figure 7-5A & B). The cement is used to fill the areas that are not in contact. The cement prevents oral fluid from flowing between the surfaces, thereby preventing bacterial invasion. Luting of a device to a tooth requires a cement of low viscosity and low contact angle to the tooth and the appliance to form a continuous film (Figure 7-5C), without the formation of voids at interface (Figure 7-5D). Voids impair the cement's ability to support and retain a prosthesis.

Porosity in powder-liquid cements is created from incorporating air while mixing powder into liquid. One study with luting agents showed that the method of mixing had no influence on the formation of small pores, but hand mixing yielded more large pores than triturator mixing. Porosity measurement of hand-mixed powder-to-liquid cements showed that polycarboxylate cement had the highest porosity, followed by zinc phosphate and GICs. Higher viscosity generally leads to more pores during mixing. If air bubbles are entrapped, masticatory forces may fracture weak appliances such as veneers. When a void-free layer is formed and hardens, one surface is wedged against another to resist the shearing stresses that might dislodge the appliance.

To choose a cement for attaching a fixed prosthesis, the key characteristics are the working time, setting time, consistency, ease of removal of excess material, and adhesion. Any cement



• **Figure 7-5** Schematic illustration of the abutment-prosthesis interfaces. **A**, Irregular surface morphology of the two surfaces to be bonded. **B**, Two surfaces pressed against each other without an intermediate layer. Note the small number of points of contact illustrated by the circles. **C**, Continuous interface when a third material, either cement or adhesive, is used as the intermediate layer. **D**, Voids generated as a result of the inability of the intermediate layer to wet the surfaces completely.

for attachment must flow under pressure and wet (spread over) the tooth and prosthetic surfaces. The internationally accepted requirements for luting cements are shown in [Tables 7-2](#). Luting cements are required to have a film thickness less than 25 μm when tested according to American National Standards Institute (ANSI)/American Dental Association (ADA) Specification No. 96 and ISO 9917-1 or 9917-2. For endodontic sealers, which are discussed later, the maximum film thickness is 50 μm per ISO 6876. The film thickness essentially reflects the consistency of the cement mixture and is affected by the size of particles and the P/L ratio. The ISO film-thickness test method requires freshly mixed cement to be placed between two optically flat surfaces, and a 150-N vertical load is applied. Seven minutes later, the thickness of the film is measured. Such samples should appear to create continuous films.

The intaglio of a crown must be cleaned before the application of luting cement. The interior surface should be carefully abraded with a stone or sandblasted with alumina abrasive. Prolonged sandblasting can deform metal margins or erode ceramic margins and should be avoided. Crowns should be thoroughly rinsed to remove debris and dried. Cementing a prosthesis to a tooth occurs in three steps after the cement is mixed, if mixing is required: cement placement, seating, and excess-cement removal.

After mixing, a luting cement should be as free of bubbles as possible, and then placed in the intaglio of a crown or bridge ([Figure 7-6, A & B](#)). The cement should coat the entire intaglio surface but fill only a portion of the intaglio. Filling the entire

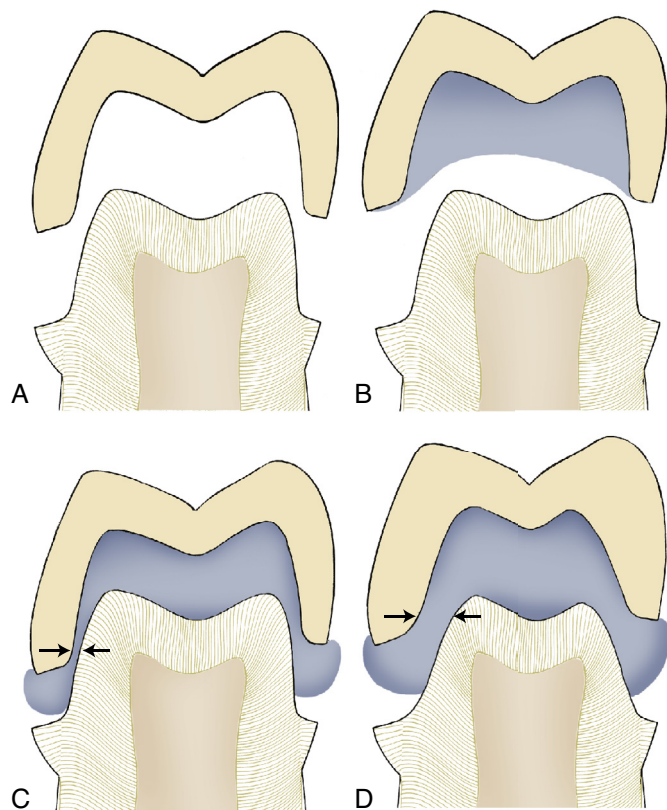
intaglio increases the risk for bubble entrapment, the time and pressure needed for seating, and the time and effort required to remove excess cement. A fixed prosthesis should be fully seated with moderate finger pressure, displacing excess cement.

Cement thickness is not the same as film thickness but refers to the actual thickness of the cement that occurs clinically between a cast crown, inlay, onlay, or veneer and the tooth structure. Lower-viscosity cements make the seating process easier. Thinner cement layers are created by applying sufficient seating force such that excess cement is expressed at the margin. Tapping the crown or vibrating the crown with an ultrasonic device may help achieve complete seating. Asking the patient to bite on a soft substance such as wood or a cotton roll also helps complete seating and expels excess cement ([Figure 7-6, C](#)). Three points on the margin should be examined with an explorer to ensure seating was complete. The design of the prosthesis should allow the cement to flow and create an even layer of cement between the prosthetic device and the tooth. However, a higher taper of the tooth preparation ([Figure 7-6, D](#)) and a lower crown height reduce retention. Cement thickness between the prosthesis and the abutment should be thin to minimize pores, maximize retention, and minimize plaque accumulation and micro-leakage between the device and the tooth.

Cement thickness plays a significant role in prosthesis retention. The thickness varies with (1) the amount of force applied during seating of the prosthesis, (2) the direction in which the force is applied to the prosthesis during seating, (3) the design of the prosthesis relative to hindering or facilitating the flow of cement, (4) the fit of the prosthesis on the prepared tooth, and (5) the inherent film thickness of the cement. An acceptable cement thickness value in the literature is between 25 and 150 μm .

CRITICAL QUESTION

Why does the technique of removing excess cement differ among the types of cements?



• **Figure 7-6** Mechanics of cementing a prosthesis. **A**, Assembly of a fixed prosthesis and respective tooth preparation. **B**, Luting agent placed in the prosthesis should cover the entire surface. **C**, Space for expelling excess cement decreases as the prosthesis reaches its final position. Arrows show the thickness of space for expelling excess cement. **D**, Higher degree of the abutment taper provides a greater space for expelling excess cement.

Excess luting cement should be present at the margin of a crown just after seating, an indication of complete cement coverage under the crown. The technique of removing excess cement depends on the properties of the cement that should be described in the instructions for use. A knotted dental floss should be run through the interproximal regions immediately after complete seating of the prosthesis to remove excess cement and create access for cement removal required in other parts of the margin.

Aqueous-based cements mature after the setting and require moisture, but not too much moisture. As a precaution, the clinician should apply a varnish coat (or a bonding agent) along the accessible margin of cemented restorations before discharging the patient. This coating should seal the margin, prevent dissolution, and avoid infiltration by food or beverages during maturation, and it may release fluoride.

A crown or bridge may be dislodged after the cement has set if the cement fractures, dissolves, or erodes, which leaves a space where plaque may accumulate, and caries may recur in the marginal opening ([Figure 7-7](#)). Care must be exercised during luting to avoid this occurrence.

Zinc Oxide–Based Cements

The zinc oxide group of cements include zinc phosphate, zinc carboxylate, and ZOE cements ([Figure 7-8](#)). Although they are less popular today, understanding these cements enables one

to appreciate the evolution of dental cements to contemporary adhesives. The acid–base reaction never progresses to completion. Therefore the hardened cements retain composite structure, unreacted powder particles in a matrix of reaction products.

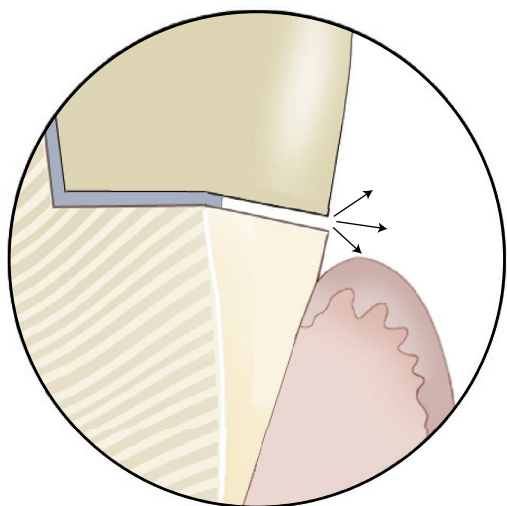
Zinc Phosphate Cement

This cement's powder contains zinc oxide (>75%) and as much as 13% magnesia (magnesium oxide) and radiopaque powder. The zinc oxide and magnesia may have been sintered, and then ground into a fine powder; the sintering intimately combines the two powders to control the setting rate. The finer the particle size, the faster the cement sets, which is true for all the powder–liquid reactions. Bismuth oxide is common as a radiopaque powder component in these cements. The water-based liquid contains phosphoric acid (38% to 59%), aluminum phosphate (2% to 3%), and sometimes zinc phosphate (0% to 10%) to adjust the setting reaction to a rate suitable for dentistry.

Critical Question

Explain why zinc phosphate cement should be mixed by increments on a cool slab.

To mix zinc phosphate cement, the powder should be dispensed first on a cool glass mixing slab and divided into six increments, usually noted in the manufacturer's instructions for use. The temperature of the glass slab should be above the dew point



• **Figure 7-7** Loss of cement at the marginal area resulting from exposure to oral fluid.

of the room; otherwise, moisture condensed on the slab will dilute the liquid, reducing the strength of the zinc phosphate cement. Next, the liquid is dispensed just before mixing to minimize the evaporation of water from the liquid. When the powder and liquid are mixed, the phosphoric acid solution (pH ~0.5) dissolves the outer surface of the particle. The dissolved zinc ions react with the aluminum phosphate ions in the liquid to precipitate a zinc alumino-phosphate gel on the remaining undissolved zinc oxide particles. The reaction between zinc oxide and phosphoric acid is exothermic and requires a strict mixing protocol to control excess heat generation. A small increment of powder is first mixed to reduce the acidity of the liquid. Subsequent increments of powder are added, and the heat also increases. Brisk spatulation for less than 20 seconds is needed for each powder increment, with all powder incorporated within 2 min to create a creamy mixture. The heat must be dissipated properly by the cool glass slab; otherwise, the reaction will accelerate and shorten the working time. Nonabsorbent paper pads should not be used. A test of “stringing” the cement before use will indicate if the mixture is too viscous for cementation.

After seating a prosthesis with a zinc phosphate cement, firm pressure and a dry field are needed until the cement sets. Excess cement in the interproximal area should be removed immediately with a knotted dental floss after complete seating. The rest can be removed after complete setting. Varnish or other nonpermeable coating should be applied at the margin to allow the cement to mature isolated from the oral fluids. If a cavity liner has been applied before the zinc phosphate cement, retention will be lower because of the smooth liner surface with less interlocking.

CRITICAL QUESTION

Why should freshly mixed zinc polycarboxylate cement be applied on the tooth preparation before the cement loses its glossy appearance?

Zinc Polycarboxylate Cement

Zinc polycarboxylate cement evolved from zinc phosphate and was the first dental cement that chemically bonded to teeth. This powder–liquid cement sets via an acid–base reaction of a powder similar to that of zinc phosphate cement with a liquid based on polyacrylic acids having a molecular weight of 30,000 to 50,000 Dalton. The acid concentration varies from 32% to 42% by weight. Zinc polycarboxylate cements set by the acid-dissolving part of the zinc oxide particles, which releases zinc, magnesium, and tin ions that bind and crosslink the carboxyl groups. The polyacrylic acid bonds to the zinc ions of the powder and to the calcium ions of the mineralized tooth. A crosslinked polycarboxylate matrix phase



• **Figure 7-8** Zinc oxide–based cement. A, Zinc-phosphate cement. B, Zinc polycarboxylate cement. C, Polymer-reinforced zinc oxide–eugenol cement.

is formed, which encapsulates the unreacted portion of the particles, as with zinc phosphate cement. Stannous fluoride may be a minor component to modify the setting time, raise the strength, and enhance manipulative properties. The fluoride released from such zinc carboxylate is minor compared with that released from the glass-ionomer cements discussed later.

The powder may be refrigerated, which will retard the reaction. However, the liquid should not be refrigerated because this will cause it to thicken. Polycarboxylate cements are mixed at about 1.5:1 powder:liquid by weight on a nonabsorbent surface. The powder should be incorporated into the liquid to create a glossy mixture, indicative of carboxylic acid on the surface for bonding to the tooth. A cool slab can be used to lengthen the working time for zinc carboxylate cement, even though the reaction is not exothermic; however, a cool slab thickens the polyacrylic acid, which hinders mixing.

A meticulously clean tooth surface is necessary to achieve adhesion and ensure intimate contact between the polycarboxylate cement and the tooth. Application of a 10% polyacrylic or maleic acid solution (10 to 15 seconds) should precede cement application, followed by rinsing with water. After cleansing, the abutment should be isolated and blotted dry to prevent contamination by oral fluids. Drying with an air syringe is acceptable, although the patient may experience discomfort if a vital tooth is not anesthetized. The outer surface of a prosthesis should be coated carefully with a separating medium, such as petroleum jelly. The separating medium prevents excess polycarboxylate cement from adhering to the crown so that excess cement can be removed when the cement hardens.

The working time for polycarboxylate cement is much shorter than for zinc phosphate cement, approximately 2.5 versus 5 min; therefore rapid spatulation and prompt seating are necessary to ensure a low cement thickness. The pH of the cement liquid is initially very low (1.7) but higher than that of zinc phosphate, and it rises rapidly as the setting reaction proceeds. During setting, polycarboxylate cement passes through a rubbery stage. Excess cement should not be removed during this stage because the cement can be pulled out from the margins, leaving a void. The setting time ranges from 6 to 8 min as required in ISO 9917-1. Because of the short working time, only crowns or short bridge spans can be cemented with zinc polycarboxylate cement. The adhesive acrylic bonds create a cement that can withstand thermal cycling, unlike zinc phosphate cement.

Zinc Oxide Eugenol and Noneugenol Cements

ZOE cements have been formulated as powder–liquid and two-paste systems. The powder–liquid combination contains zinc oxide powder and eugenol liquid. The two-paste system includes a base paste containing zinc oxide powder, and the eugenol is in the accelerator (or catalyst). The ZOE setting reaction starts with water present in the tooth or the eugenol solution hydrolyzing the zinc oxide to form zinc hydroxide. The zinc hydroxide and eugenol chelate and solidify. The reaction proceeds more rapidly in a warm, humid environment, such as inside a tooth. When zinc acetate dihydrate is included in the powder, the reaction is faster; zinc acetate is more soluble than zinc oxide or hydroxide. Acetic acid in the eugenol solution also accelerates the dissolution of zinc oxide. The setting reaction is slower for the other zinc oxide cements. A wide variety of ZOE cements are available, with compressive strengths ranging from 3 to 55 MPa. Finer powders increase the strength of the resulting cement.

The versatility of ZOE is reflected in ISO 3107:2011 (ANSI/ADA Standard No. 30), which lists four clinical types of ZOE

cement: (1) temporary cementation, (2) long-term cementation of fixed prostheses, (3) temporary fillings and thermal insulating bases, and (4) intermediate restorations. ZOE cements are also used as root canal sealers and periodontal dressings. Temporary ZOE restorations are expected to last a few weeks. The antimicrobial attribute of ZOE is a benefit compared with glass-ionomer cements or resin composites. However, ZOE cements can cause pulpal necrosis; therefore ZOE should not be used directly on pulp. Indirectly used, ZOE has a sedative effect by sealing the dentinal tubules against the ingress of oral fluids until a more permanent restoration can be fabricated and cemented.

Intermediate-duration ZOE cements serve as a restorative material for about 1 year. To achieve the properties necessary for this use, a stiff, putty-like restorative consistency must be used (high P/L ratio). The higher the P/L ratio, the faster the material sets. A cool glass mixing slab slows the setting, which should be above the dew point to avoid moisture condensation and dilution of the cement.

An excellent application for these ZOE cements is for temporary or provisional (short-term or intermediate-term) luting of provisional fixed prosthodontics. Long-term ZOE luting cements are somewhat difficult to manipulate because their film thicknesses are high, and excess cement is difficult to remove; therefore long-term ZOE luting cements should never be used for temporary cementation. ZOE cement is used for implant superstructure cementation, where more retentive cements could lead to damage of the supporting implant if retrieval is required. The consequence of the less adhesive cement is potential loosening of the implant prosthesis.

To improve the strength of ZOE cements, part of the eugenol liquid has been replaced by orthoethoxybenzoic acid and alumina added to the powder. Another system, called *polymer-reinforced ZOE*, incorporates a powder containing 20 to 40 wt% fine polymer particles and zinc oxide particles treated with carboxylic acid. Residual eugenol is thought to interfere with the proper polymerization of resin-based composites or cements; therefore some carboxylic acids have been used to replace eugenol and produce a ZOE-like material. Such products are called *zinc oxide–noneugenol cements*. The compressive strength of these improved ZOE cements is acceptable, but their strength values are inferior to those of glass-ionomer and resin cements (Table 7-4).

Glass-Ionomer Cement

Glass polyalkenoate cement is the proper designation for specialized glass powders that react with polyacrylic acid. However, *glass ionomer*, *glass-ionomer cement*, and *GIC* are recognized as acceptable names within the dental profession. The glass-ionomer cements are an improvement over the predecessor silicate cements because they include the bonding mechanism found in the zinc carboxylate cement with glass powder. The result is a superior and versatile material that is adherent, translucent, and fluoride releasing. GICs have been used for (1) the esthetic restoration of anterior teeth (e.g., class III and V sites), (2) adhesive cements for fixed prostheses and orthodontic appliances, (3) intermediate restorations, (4) pit and fissure sealants, (5) cavity liners and bases, and (6) core buildup materials. The GICs are classified by variations in powder composition and particle size to achieve the desired function, as follows:

- Type I: Luting crowns, bridges, and orthodontic brackets
- Type II a: Esthetic restorative cements
- Type II b: Reinforced restorative cements
- Type III: Lining cements and bases

Chemistry and Setting

The glass powders for GIC always contain silica, calcia, alumina, fluoride, and other oxides (Table 7-5). Higher-atomic-number metal oxides (baria, strontia) are included in the glass formulas to increase radiopacity. During melting, the raw materials are homogenized into an amorphous glassy mass at temperatures between 1100° and 1500 °C. After the molten mass is quenched, the glass is ground into a powder, with average particle sizes ranging from less than 10 to about 50 μm , depending on the indication. Coarser powders are used for restoratives, and finer particles are used for cementing devices or pulpal protectant products. These glass powders for polyalkenoate cements are soluble in the polyacrylic acids.

The first aqueous GIC solutions contained 40% to 50% polyacrylic acid, but such liquids were viscous and had a short shelf life because they gelled. Current glass-ionomer liquids contain mixtures of copolymers of itaconic, maleic, or tricarboxylic acids (Figure 7-9). Tartaric acid is used as a rate-controlling additive in the GIC liquid to improve handling, decrease viscosity, and increase working time. Tartaric acid also shortens the setting time (Figure 7-10) by “sharpening” the setting curve and extends the shelf life before the liquid gels. Adding 5% to 10% tartaric acid enables the use of lower-fluoride-content glasses, which makes the restoratives more translucent and esthetic. Fluoride in glass can cause phase separation within the glass particles, which creates opacity.

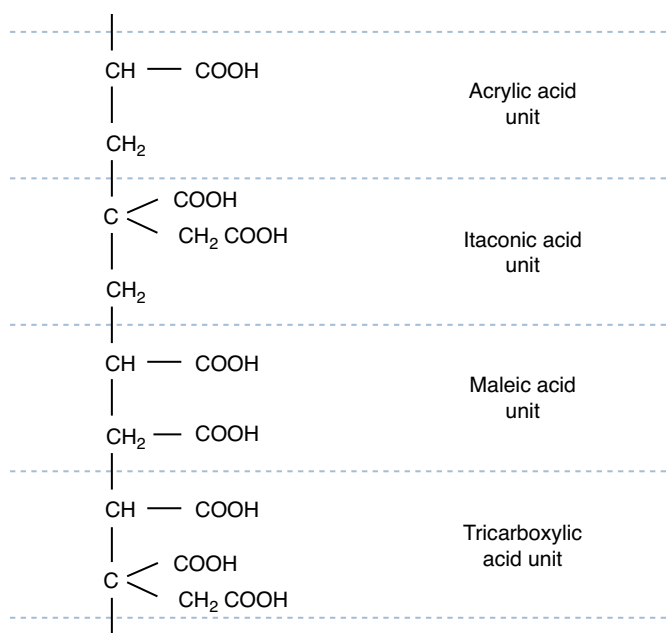
When the GIC powder and liquid are mixed, the acid starts to dissolve the glass, releasing calcium, aluminum, sodium, and fluorine ions into the liquid. The high aluminum content is the key to the glass reactivity with polyacrylic acid. The undissolved portion of the glass particles is sheathed by a silica-rich gel formed on the surface of the glass particles when the ions are leached. The polyacrylic acid chains crosslink with the calcium ions and aluminum ions. Sodium and fluorine ions of the glass do not participate in the crosslinking of the cement. The set GIC consists of undissolved glass particles with a silica gel coating, embedded in an

amorphous matrix of hydrated calcium and aluminum polysalts containing fluoride ions. Figure 7-11 shows the stylized structure of set GIC. Glass ionomers bond to tooth structure by chelation of the carboxyl groups of the polyacrylic acids with the calcium in the apatite of the enamel and dentin, like that of polycarboxylate cement. Figure 7-12 is a micrograph of set GIC.

A specialized GIC known as a *water-settable glass ionomer* is formulated with freeze-dried polyacrylic acid blended with the glass powder. The powder is mixed with water or an aqueous solution containing tartaric acid. This type of GIC has an extended working time because additional time is needed to dissolve the dried polyacrylic acid in water to initiate the acid–base reaction.

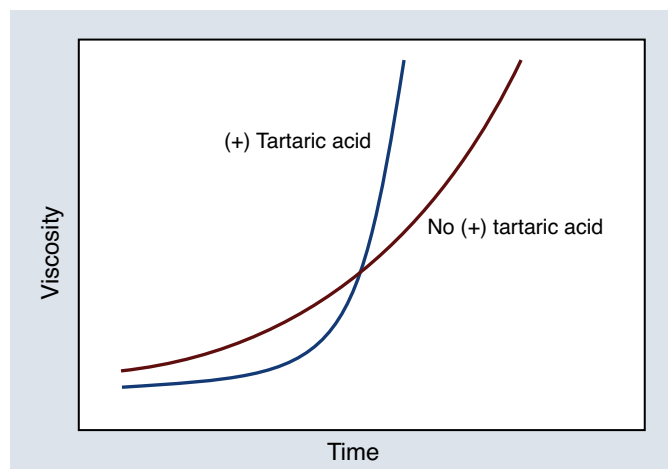
CRITICAL QUESTION

Identify two critical roles of water in the setting of conventional GIC, and discuss their influence on the properties of the set GIC.

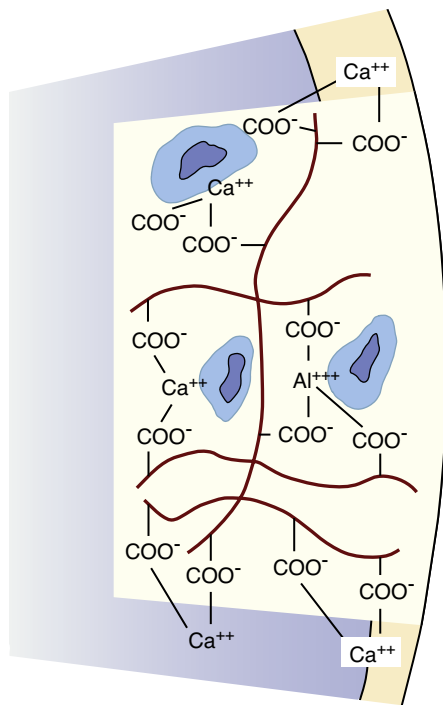


• **Figure 7-9** Structure of various types of alkenoic acids that make up polyacids of glass-ionomer cements.

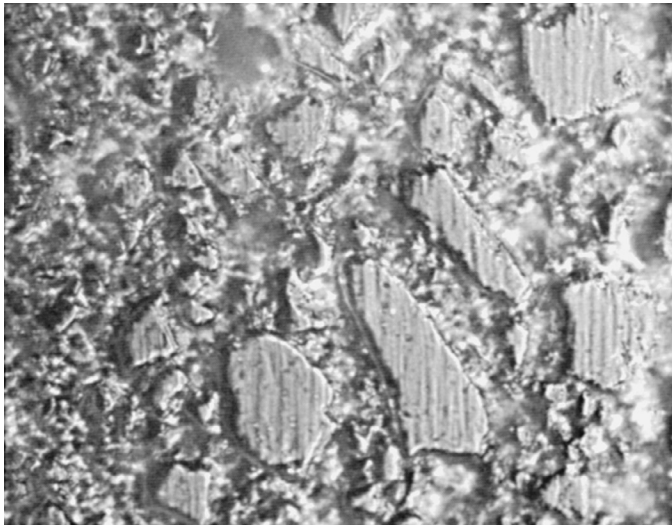
TABLE 7-5 Nominal Compositions of Glass-Ionomer Cement Powders (wt%)						
Compound	A	B	C	D	E	F
SiO ₂	36	20–30	41.9	35.2	34	32
Al ₂ O ₃	36	10–20	28.6	20.1	45	32
AlF ₃			1.6	2.4		
CaF ₂			15.7	20.1		
NaF			9.3	3.6		
AlPO ₄			3.8	12.0		
F	9	10–15			9	8
Na ₂ O	7	1–5				7
La ₂ O ₅						3
BaO		10–20				
CaO	14	10–20				13
SrO					11	
P ₂ O ₅	5	1–5			1	5



• **Figure 7-10** Effect of tartaric acid on the viscosity–time relationship for a glass-ionomer cement during setting.



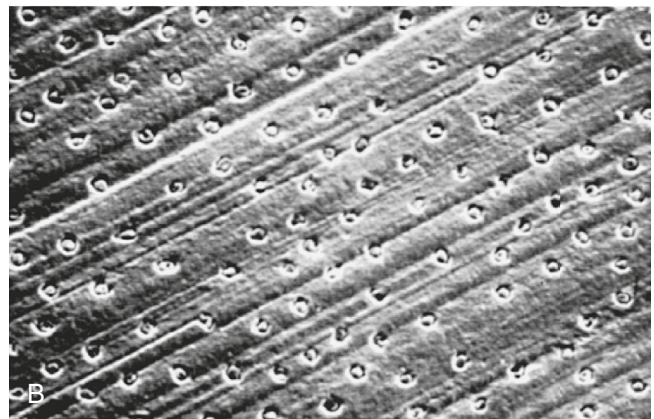
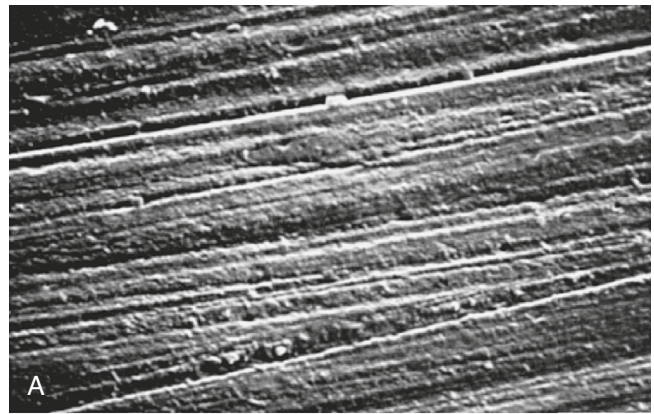
• **Figure 7-11** Diagram depicting the structure of a glass-ionomer cement. The solid blue particles represent unreacted glass particles, surrounded by the gel (light blue shaded structure), that form when Al^{3+} and Ca^{2+} ions are leached from the glass as a result of attack by the polyacrylic acid. The Ca^{2+} and Al^{3+} ions form polysalts with the COO^- groups of the polyacrylic acid to form a crosslinked structure. The carboxyl groups react with the calcium in enamel and dentin.



• **Figure 7-12** Photomicrograph of a set glass-ionomer cement showing unreacted particles surrounded by the continuous matrix.

Clinical Manipulation

Before using GIC for luting, the surface of the prepared tooth must be clean, uncontaminated by saliva or blood, and dry but not desiccated deep into the tubules. A pumice slurry can be used to remove the smear layer produced by cavity preparation.



• **Figure 7-13** Prepared dentin surfaces. **A**, Freshly prepared surface with smear layer. **B**, After cleansing with polyacrylic acid, the smear layer is removed, yet the tubules remain plugged.

Alternatively, the tooth may be etched (conditioned) with phosphoric acid (34% to 37%) or an organic acid—like polyacrylic acid (10% to 20%) for 10 to 20 seconds, followed by a 20- to 30-second water rinse. **Figure 7-13** shows the smear layer and the smear layer removal after a 10-second swabbing action with a 10% polyacrylic acid solution. For cases where the residual dentin thickness from the pulp is less than 0.5 mm, a calcium hydroxide or tricalcium silicate liner is needed to ensure the GIC acidity does not affect the pulp. The need for protection from the acidity of the water-based cements is seen in **Table 7-6**. After 24 hours, the pH values of these cements have risen from 2 to 6.

A nonabsorbent paper pad or a cool, dry glass slab may be used for mixing GIC. A cool glass slab will retard the reaction, which extends the working time. Like the zinc oxide cements, the slab should not be colder than the dew point of the room temperature to avoid water condensation and dilution of the liquid. The powder and liquid should be dispensed just before mixing is begun; otherwise, evaporation of water increases the acidity of the liquid. The powder should be rapidly spatulated into the liquid in less than 45 seconds, or as prescribed in the instructions for use. Normally, one-half of the powder is mixed into the liquid for 5 to 15 seconds; then the remaining powder is quickly added and mixed by folding the cement on itself until a uniform and glossy appearance is observed. A glossy appearance is critical because this indicates that unreacted polyacid is present for bonding to teeth. A dull appearance indicates that the setting reaction has progressed too far.

The viscosity of the mixed GIC varies widely among manufacturers from low to very high. The variations are achieved by varying the particle-size distribution and P/L ratio. Coarser particles (about 50 μm average) are used for the viscous, restorative indications, and fine glass particles (about 15 μm) are used for cementing.

Some glass ionomers are supplied in capsules containing preproportioned powder and liquid (Figure 7-14). The capsules are convenient and offer a consistent P/L ratio with less variation than hand spatulation. The seal of the capsule is broken, and the capsule is placed in a triturator for the time and speed given by the manufacturer. Some capsules are designed with a nozzle for injection directly into the prepared tooth cavity or fixed prosthesis.

With any glass-ionomer cement, a protective liner (i.e., $\text{Ca}[\text{OH}]_2$) should be used if the preparation is estimated to be closer than 0.5 mm to the pulp chamber. Glass-ionomer restoratives pose a lesser pulpal hazard than when used as luting cements because the luting cements are mixed with a low P/L ratio and remain acidic for a longer time. For luting, GIC is applied with a plastic instrument to coat the entire intaglio surface of the prosthesis before seating. Excess cement can be removed immediately after seating or when prescribed in the instructions for use. No surface protection of the cement is needed during the

initial setting, but a protective coating should be applied after the removal of excess cement to avoid excess water sorption. For GIC restorations, the surface of fresh GIC should be covered with a plastic matrix for about 5 min to avoid excess water sorption during the initial setting. Otherwise, saliva will dilute the matrix-forming cations and anions and destroy the hydrated matrix, creating a weak restorative. When the plastic matrix is removed, the surface must be protected with varnish or petrolatum while the excess GIC is removed from the margins. Surface finishing of GIC restorations must be carried out after the cement sets and without excessive drying. Before dismissing the patient, GIC restorations should again be coated with varnish or petrolatum. If these recommended procedures are not followed, the surface inevitably becomes chalky or crazed, such as in the restorative shown in Figure 7-15.

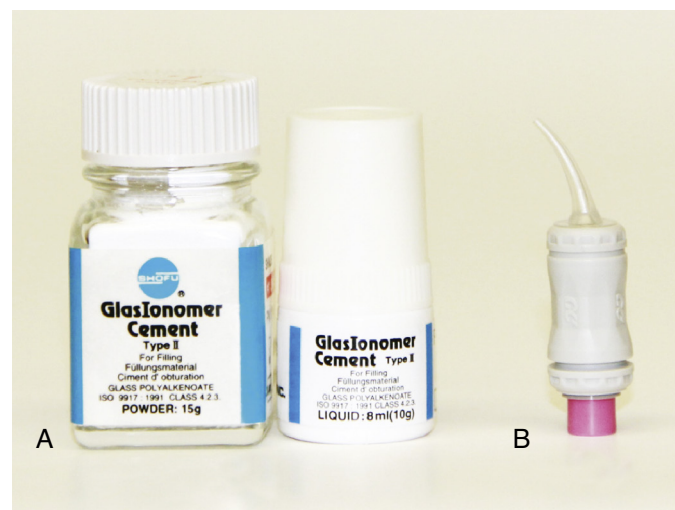
Glass ionomers have served patients well because of their dimensional stability and persistent fluoride release (Table 7-7), lasting for 30 days after setting. Although in vitro studies have shown the ability of the glass-ionomer restorations to inhibit enamel and dentin demineralization, not all clinical studies have confirmed the effectiveness of GIC over nonfluoridated materials. GIC restoratives are more vulnerable to wear and have lower fracture toughness than composite restorations.

TABLE 7-6 pH Powder–Liquid Acid–Base of Cements

Time	GLASS IONOMER			
	Zinc Phosphate	Zinc Polycarboxylate	Polyacid Liquid	Water Settable
2 min	2.1	3.4	2.3	1.8
5 min	2.6	4.0	3.3	2.0
10 min	3.1	4.4	3.8	3.4
15 min	3.3	4.8	3.9	3.9
60 min	4.3	5.1	4.6	4.8
24 h	5.5	6.0	5.7	6.0

Metal-Reinforced Glass-Ionomer Cement

Metal powders have been incorporated into glass-ionomer cements with the objective of faster setting and perhaps replacing amalgam. The metallic fillers can be silver alloy powder, such as the alloys used in amalgams, termed *alloy admix*, or particles of silver sintered to glass, known as *cermet*. Metal fillers make the GIC grayish but more radiopaque. More fluoride is released from the admix type because the alloy particles are not bonded to the glass. Less fluoride is released from GI cermet because a portion of the glass particle is coated with metal. All the procedures that apply to conventional GIC apply to metal-reinforced GIC. The faster setting, adhesion, and fluoride release from metal-reinforced GIC are useful for the following applications:



• **Figure 7-14** Two powder–liquid type II restorative glass-ionomer cements. **A**, Two-bottle system for hand mixing. **B**, Capsule for trituration (GC Fuji Triage capsule).



• **Figure 7-15** Crazed surface on glass-ionomer restorations that resulted from inadequate protection of the material during maturation. (Courtesy Dr. Saulo Geradeli.)

TABLE 7-7 Cumulative Fluoride Release From Various Glass-Ionomer Products

Cement Type	FLUORIDE RELEASED (μg)	
	14 Days	30 Days
Cermet	200	300
Type II glass ionomer	440	650
Type I glass ionomer	470	700
Glass-ionomer liner (conventional)	1000	1300
Glass-ionomer liner (light-cured)	1200	1600
Alloy admix glass ionomer (silver alloy admix)	3350	4040

TABLE 7-8 Properties of Restorative Glass-Ionomer Cements

	Compressive Strength (MPa)	Diametral Tensile Strength (MPa)	Hardness (KHN)
Glass ionomer (Type II)	196–251	18–26	87–177
Cermet	176–212	19–22	30–45
High-viscosity glass ionomer	301	24	108
Hybrid ionomer	202–306	20–48	64–85

(1) core buildups of teeth to be restored with cast crowns, (2) restoratives on occlusal surfaces of primary molars with stainless-steel crowns, and (3) cementing pins and other retentive forms. The metal-reinforced GICs have limited use as an alternative to amalgam or composite for posterior restorations because they are weaker than resin composite core materials and other GICs (Tables 7-8 and 7-9).

CRITICAL QUESTION

For the atraumatic restorative treatment technique, why is a high-viscosity GIC the most appropriate material?

High-Viscosity Glass-Ionomer Cement

Atraumatic restorative treatment (ART) is a preventive and restorative caries-management concept developed for dentistry in regions of the world that do not have infrastructure such as electricity or piped water systems. Glass-ionomer cements are a natural choice for ART because of their adhesion and fluoride release. High-viscosity GICs have been developed for this purpose with smaller particle sizes and using a higher P/L ratio, which increases the compressive strength (Table 7-8).

The clinical steps in the ART procedure are as follows: (1) isolating the tooth with cotton rolls, (2) accessing the carious lesion with hand instruments, (3) removing the soft tissue with an

TABLE 7-9 Fracture Toughness of Glass-Ionomer Materials and Selected Restorative Materials

Type of Material	Fracture Toughness ($\text{MPa}\cdot\text{m}^{1/2}$)
Conventional GIC (luting) ³	0.27–0.37
Metal-modified GIC (admixed) ⁵	0.30
Metal-modified GIC (cermet) ⁵	0.51
High-viscosity GIC ⁶	0.45–0.72
Conventional GIC (restoration) ⁴	0.72
Resin-modified GIC (luting) ³	0.79–1.08
Compomer (restoration) ²	0.97–1.23
Resin cement ³	1.30
Resin-modified GIC (restoration) ⁵	1.37
Amalgam ¹	0.97–1.60
Hybrid composite ²	1.75–1.92

¹Lloyd CH, Adamson M. The fracture toughness (K_{IC}) of amalgam. *J Oral Rehabil* 12:59, 1985.

²Adrian Yap UJ, Chung SM, Chow WS, Tsai KT, Lim CT. Fracture resistance of compomer and composite restoratives. *Oper Dent* 29:410, 2004.

³Mitchell CA, Douglas WH, Cheng YS. Fracture toughness of conventional, resin-modified glass-ionomer and composite luting cements. *Dent Mater* 15:7, 1999.

⁴Bonilla E, Mardirossian G, Caputo AA. Fracture toughness of various core build-up materials. *J Prosthodont* 9:14, 2000.

⁵Kovarik RE, Muncy MV. Fracture toughness of resin-modified glass ionomers. *Am J Dent* 8:145, 1995.

⁶Yamazaki T, Schrickler SR, Brantley WA, Culbertson BM, Johnston W. Viscoelastic behavior and fracture toughness of six glass-ionomer cements. *J Prosthet Dent* 96:266, 2006.

GIC, glass-ionomer cement.

excavator, (4) using a weak acid to condition the tooth (enhance chemical bonding), and (5) placing a high-viscosity GIC using finger pressure. The survival rate of partially and fully retained single-surface restorations on permanent teeth was reported as 88% after 3 years. Another study followed restorations in two groups of children: (1) high-viscosity GIC placed by the ART procedure and (2) amalgam restorations. The cumulative survival rates after 6.3 years for ART and amalgam restorations were 66% and 57%, demonstrating the usefulness of the ART procedure.

In a general practice office, electricity and water are available, but the same ART procedures can be used, augmented by rotary instruments. One study compared the survival of high-viscosity GIC using the ART procedure and conventional cavity preparation with rotary instruments; no statistical difference was observed between the two methods for class I preparations after 2 years. High-viscosity GICs have been used for core buildup, primary tooth filling, non-stress-bearing restorations, and intermediate restorations. Short-term clinical studies confirmed that high-viscosity GICs are suitable alternatives to amalgam in class I and class II restorations in primary teeth. The capsulized packaging of high-viscosity GIC (Figure 7-16) is convenient for trituration.

Orthodontic bands are commonly cemented with GIC. Band removal is easier with GICs because the use of a desiccating air spray will weaken the cement. Glass ionomers have also been used for pit and fissure sealing.



• **Figure 7-16** Two high-viscosity glass-ionomer cements.

Resin Cements

Resin cements are low-viscosity versions of resin-based composites. These cements have a matrix of methacrylate monomers with dispersed fillers. Silane coating is required on the filler particle surfaces to bond them to the monomers during polymerization for a durable, wear-resistant material. Polymerization of the resin cement can be by self-, light- or dual-cured mechanisms. Most resin cements for adhering devices are dual-cured materials. Dual- or self-cured cements are used for prostheses made with medium- or high-opacity materials. For dual-cured cements, blue light initiates the curing at the margins, and the self-cure progresses over time. The light-cured resin cements are indicated for cementing ceramic veneers and direct bonding of ceramic or polymeric orthodontic brackets. Because of light attenuation by the translucent prostheses, longer light exposure is often required than with direct composites. However, the duration of light exposure should be minimized to avoid heating the pulp. Many brands are available worldwide, which vary widely in physical properties (Figure 7-17).

Composition and Setting

Resin cements, like resin-based composite, require the same bonding systems as resin-based composites for adhesion to teeth. Many bonding systems are available, which vary in the steps needed. The one-, two-, and three-component systems were discussed in Chapter 6, *Classifications by Clinical Steps*. The one-component system combines etching and priming. Bonding systems, like the resin cements, may be self-, dual-, or light-cured materials, but all incorporate at least one hydrophilic monomer. Thirty hydrophilic monomers have been used, each with a methacrylate functionality,



• **Figure 7-17** Commercial resin cements. **A**, A hand-mixing paste-paste dual-cured system for temporary prostheses. **B**, A single-component light-cured system for porcelain veneers. **C**, A paste-paste dual-cartridge dispensing system that requires hand mixing. **D**, A powder-liquid capsule system that is triturated. **E**, Two paste-paste dual-cartridge systems that require static mixing; the top one requires a bonding agent, and the bottom one is self-adhesive. **F**, A liquid-liquid system.

to infiltrate the dentinal collagen and establish a micromechanical bond. Typically, these monomers are acidic or amide formulas in a water-miscible solution. Examples are HEMA, 4-META, carboxylic acids, and an organophosphate (e.g., 10-methacryloyloxydecamethylene phosphoric acid [MDP]). For systems that require a bonding agent, the resin primers partially infiltrate the collagen fibrils that have been demineralized by acid etching. The resin tags fill the space to reduce adverse pulpal responses from the osteoblastic processes in the tubules.

Self-cured and dual-cured resin cements contain two components (base and catalyst) that require mixing. Components are mixed on a paper pad for 20 to 30 seconds or two pastes can be mixed when dispensed through a dual-chambered syringe through a static mixing tip. Chemical activation is slower than with light curing and provides extended working time. In dual-cured cements, light-curing becomes dominate setting mechanism when the cement is exposed to a curing light. The most esthetic resin cements are light-cured only, and their color stability over time is better than the dual-cured resins.

Some bonding agents are called “universal” bonding agents by the manufacturer. Most universal bonding agents can be used with total, self-, and selective etching before placement of dual- or self-curing cements. Some universal adhesives release fluoride, and some are two-part liquids that require mixing. The adhesive agent may also be used as a primer on metal and ceramic-based restoratives.

Not all resin cement systems require a bonding agent. One system based on 4-META uses liquid monomers and catalysts without any traditional inorganic fillers and relies on mixing with various amounts of polymer beads to adjust the viscosity of the cement for intended applications. This cement eliminates the steps of etching, priming, and bonding and allows the clinician to bond prostheses directly to clean abutments. These cement systems rely on modified dimethacrylate monomers with acid-containing side chains, such as phosphoric acid, attached as pendant groups. Upon contact with the tooth surface, the acidic group binds with calcium in the hydroxyapatite to bond to the tooth.

The current self-adhesive resin cements are two-part systems: liquid–powder and paste–paste. For the paste–paste system, one component is composed of the conventional monomers used in resin-based composites and acid-leachable fillers, similar to those used in GICs. The other component contains acid-functional monomers (Figure 6-4) to achieve demineralization and bonding to the tooth surface, with inert fillers. Initiators for polymerization are distributed between components. Only the acidic monomers on the surface of the mixture contribute to etching and bonding of the cement to tooth surface, as in GICs. The remaining acidity of the mixture is neutralized by the leachable glass. This acid–base reaction constitutes the recurrent setting reaction and releases fluoride. The setting mechanisms also qualify them as dual-cured materials.

The self-adhesive resin cements usually show lower bond strength values than non-self-adhesive resin cements in microtensile or shear testing. Unlike phosphoric acid, the acidic monomers that etch and promote bonding of the self-adhesive resin cements do not etch enamel. Therefore for enamel bonding, phosphoric acid etching is needed.

Clinical Manipulation and Evaluation

Liquid–powder formulations are often packaged in capsule form and mixed by trituration (Figure 7-17, *D*). Two-paste resin systems are often sold with a static mixer tube to use on the end of a two-barrel syringe; the static mixer dispenses a mixed cement (Figure 7-17, *E*). Static mixing or trituration of capsules has largely replaced hand mixing. Static mixing is convenient and does not mix air into the cement, unlike hand mixing. The mechanism of static mixing is discussed in [Chapter 13, Manipulation of Impression Materials](#).

For bonding inlays or crowns, a separate phosphoric acid–etching of the enamel margins improves marginal sealing and adaptation. However, phosphoric acid decreases bond strength to dentin because the viscous cements cannot penetrate a demineralized collagenous matrix created by phosphoric acid. However, the self-adhesive resin cements have fairly strong bonds to dentin, despite the lack of formation of the classical hybrid layer shown for enamel bonding.

The chemical and physical properties of self-adhesive resin cements reported in the literature show that self-adhesive resin cements may be expected to perform as well as other resin-based and non-resin-based dental cements; however, few long-term studies are available. Nonetheless, the handling properties of these materials appear to be excellent, and their acceptance by the profession is increasing.

The monomers in uncured resin cements are irritating to the pulp. To prevent the infiltration of irritants, pulp protection with a liner is important when the thickness of the remaining dentin is less than 0.5 mm. The procedure for preparing the tooth remains the same for each resin system, but the treatment of the prosthesis differs depending on the prosthesis material, as described next.

CRITICAL QUESTION

Why does the treatment of the surface of the prosthesis differ by the type of resin cement used?

Metallic Prostheses

When bonding a base metal prosthesis, the intaglio should be roughened by electrochemical etching or grit blasting. Air blasting of metal surfaces with silicate-coated particles leaves a

silicate-embedded area that can be treated with silane to improve bonding metals with resin cements. The bond-strength values are similar for metals prepared by grit blasting and electrochemical etching. Some bonding systems include a metal primer to promote adhesion. Oxide formation on the surface of base metals increases the bond strength when a resin cement containing MDP or 4-META is used. However, high-noble-metal dental alloys lack stable surface oxides. The bonding of noble-metal prostheses is enhanced by a thin (about 0.5 μm) layer of tin electroplated on the prosthesis by a dental laboratory. When heated, a layer of tin oxide forms, which is more adhesive to the cement.

Polymeric Prostheses

Polymer-based prostheses, including polymeric veneers, must be grit-based on the intaglio to increase the roughness for mechanical adhesion. Some polymer prostheses systems have a special adhesive to be used for bonding, based on the same monomer that is used to fabricate the prosthesis. A 30-min surface treatment with special adhesive must be allowed for adequate penetration of the adhesive into the polymer prostheses before cementing.

Ceramic Prostheses

Early ceramic prostheses often fractured when nonadhesively luted with the traditional zinc oxide–based cements. The bonding agents of resin cement are now used to fill the surface flaws in the ceramic and have reduced the fracture of ceramic prostheses. Resin cement may be partially seen through a translucent ceramic prosthesis, such as ceramic veneer, and therefore influence the esthetics. Usually several shades of light-cured resin cements are available that enable the clinician to optimize esthetics with ceramic restorations. Some products include water-soluble try-in gels with the same shades as the cements. The try-in gels are applied like a cement, and then the prosthesis is provisionally seated and examined in situ for esthetic appearance. This process can be repeated with various try-in gel shades until the clinician and patient are satisfied with the esthetic appearance. After the cement shade has been selected, the try-in paste must be thoroughly removed from the tooth and the prosthesis. The cementation process is completed using a cement with the same shade as the selected try-in gel.

A variety of ceramic materials are used for prosthodontics, and they vary in composition and translucency. The porcelain and lithia disilicate materials contain glass, so these prostheses are prepared by etching with hydrofluoric acid (HF), usually by the dental laboratory. Then the etched ceramic is silanated to enhance adhesion to the resin cement. Zirconia and alumina restoratives are silica-free, acid-resistant, polycrystalline ceramics. Without the silicate glass phase, HF etching and silane application are not useful for bonding. These polycrystalline ceramic restorations must be air abraded with alumina (not silica), and then coated with a bonding agent containing MDP. Grit blasting with silicate-coated alumina particles deposits silica on the zirconia or alumina surface to help with silanization and bonding.

Orthodontic Brackets

Mechanical and chemical adhesion to metal orthodontic devices and teeth are important for the prevention of premature debonding. Bonding of orthodontic brackets requires proper isolation and etching of the enamel surface to secure the bond between the tooth and the bracket. The tooth-facing side of the bracket requires some means of mechanical retention, such as the metal mesh of the metal bracket or other retentive dimples or ridges

on ceramic or polymer brackets. Additional surface treatment depends on the class of materials used in the brackets. Ceramic bracket bases are commonly precoated with an organosilane, like those used to bond inorganic fillers within the resin matrix of resin-based composites. Polycarbonate brackets are primed with a solvent containing methylmethacrylate monomer. When treatment is completed, removal of the appliances should occur at the tooth–cement interface or, less preferably, at the cement–bracket interface, but not within the tooth enamel.

CRITICAL QUESTION

What are the advantages of incorporating polymerizing resin in the GICs?

Combination Cements

Cements may have unique properties created by substituting or incorporating ingredients. For instance, fluoride release and curing on command (light curing) are desirable for clinicians. Some noted developments in combination cements are discussed in this section.

Resin-Modified Glass-Ionomer Cement

RMGIs are also referred to as *hybrid ionomers* (Figure 7-18). These cements contain water-soluble polymerizable monomers in a liquid, usually a water solution of polyacrylic acid, 2-hydroxyethyl methacrylate (HEMA), and polyacrylic acid–modified methacrylate. Catalysts, such as diphenyliodonium chloride (DPICI), are included. This type of cement has a longer working time and is less sensitive to water contamination than conventional glass-ionomer cement.

The monomers in hybrid glass-ionomer cements make the cements more translucent than glass ionomer and therefore more suitable for restorative indications. The fluoride release and the higher diametral tensile strengths over glass-ionomer cements (Table 7-8) make the hybrid GICs more desirable for restoratives. The hybrid ionomers have a higher tensile strength that is attributed to their lower elastic modulus imparted by the resin component.

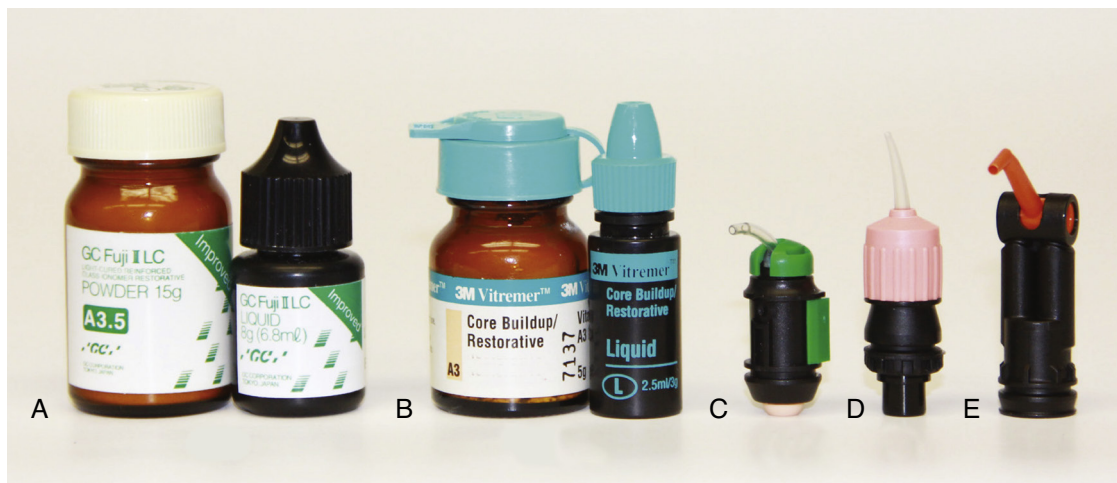
As a powder–liquid system, the liquid component comprises lower water and carboxylic acid contents than that of GIC. The powder contains fluoroaluminosilicate glass particles and initiators for light curing and/or chemical curing monomers in the liquid.

The incorporation of polymerization of the methacrylate groups makes RMGI a dual-cured cement. The acid–base reaction begins upon mixing but continues after the monomer polymerizes. A tri-cured cement has both chemical and light activation that are included with the hybrid cement. The carboxylate groups in hybrid ionomer cements bond to tooth structure as in other GICs, and the monomers form an amorphous layer at the cement–dentin interface, with some resin infiltration into the etched dentin for added adhesion. Higher bond strengths have been measured for hybrid ionomer cements than for conventional glass ionomers. The higher bonding to teeth may occur because of better micromechanical interlocking to a roughened tooth surface. The adhesion of the GIC component of hybrid ionomers to dentin reduces the probability of gap formation at gingival margins. This feature helps compensate for the polymerization shrinkage of an overlying resin composite restoration placed on a hybrid ionomer cavity base.

Clinical indications for hybrid ionomers include cavity liners/bases, fissure sealants, core buildups, adhesive for orthodontic brackets, repair material for damaged amalgam cores or cusps, and restoratives. Direct pulp capping is contraindicated. For any indication, surface conditioning of the tooth structure with a mild acid is important for bonding the resin component. Placing a hybrid ionomer, and then a resin-based composite is the so-called “sandwich technique.” This technique combines the fluoride release of a glass ionomer and the esthetics of a composite restoration and is recommended for class II and V composite restorations when individual patients are at a moderate to high risk for caries.

Low-viscosity hybrid ionomers or conventional GICs have been used for fissure/sealant indications. The retention rate of glass-ionomer sealants was poor after 1 year, but patches of glass-ionomer cement that remained within the fissures were effective in preventing caries.

Some hybrid ionomer cements are marketed based on the unique filler properties and their ability to flow or to not flow, the latter allowing “stacking.” Marketing terms such as “S-PRG” and “Giomer” are unique terms from manufacturers that indicate a glass-ionomer filler. Some hybrid ionomer cements also contain nonreactive filler particles, which lengthen the working time, improve the early strength, and reduce sensitivity to moisture during setting. The use of nonreactive filler particles along with less carboxylic acid available for bonding to tooth structure; therefore a dentin bonding system is needed.



• **Figure 7-18** Representative resin-modified glass-ionomer cements. **A and B**, Two-bottle powder–liquid system. **C**, Photac Fil Quick Aplicap. **D**, GC Fuji Plus Capsule. **E**, Ketac Nano, a paste–paste system using static mixing.

A few reports of adverse effects have been attributed to hybrid ionomers that include HEMA in the formula. HEMA can cause pulpal inflammation and allergic contact dermatitis. Therefore hybrid ionomers are not as biocompatible as conventional glass ionomers. The HEMA in hybrid ionomers increases water absorption over time, with concurrent expansion of up to 8 vol%. The expansion has been linked to the fracture of all-ceramic crown restorations when hybrid ionomers were used for core buildup or luting cement. Dental personnel may be at risk from adverse effects such as contact dermatitis and other immunological responses.

CRITICAL QUESTION

How does compomer differ from resin-based composite?

Compomer

Compomer is a light-cured material that integrates the fluoride-releasing capability of glass ionomers with the durability of composite resins in a one-paste restorative resin. As a restoration, compomer restorations perform better than resin-modified glass ionomers but are inferior to hybrid composites. They contain nonreactive inorganic filler particles, reactive silicate glass particles, sodium fluoride, a polyacid-modified monomer (e.g., di-ester of 2-hydroxyl methacrylate with butane carboxylic acid [TCB]), and photo activators. Compomers are usually one-paste materials for restorative applications (Figure 7-19).

Single-component compomer cements are water-free and are packaged in moisture-resistant blister packs. Compomers set by a polymerization reaction, and then absorb water from the saliva to initiate the slow acid–base reaction between the acidic functional groups and silicate glass particles. The product of the acid–base reaction becomes the source of fluoride release. However, restorative compomers release less fluoride than GICs and hybrid ionomers. Compomer pastes require a dentin-bonding agent prior to their placement as a restorative because they do not contain water to be self-adhesive like GICs or hybrid ionomers. The tooth structure should be etched and followed by the dentin-bonding agent before placing the compomer. The bond strength of paste compomers to tooth structure using a dentin-bonding agent is like that of hybrid ionomers. The restorative compomer materials are mainly used in low-stress-bearing areas, such as class III and V cavities, as an alternative to glass-ionomer restoratives or resin-based composites. Together with one-bottle adhesives for

bonding, compomers are also used for treating class I and class II lesions in the primary dentition because of their fluoride-releasing potential. Compomers are finished just like resin composites.

In a 24-month clinical study of fissure sealants, compomers performed as well as composite resin sealants, although their marginal integrity was less. Compomers perform as well as composite resins for class I and II restorations. However, the color stability of compomers is a problem, likely caused by water absorption and staining by food. Compomers have been used for bonding orthodontic bands and brackets because of their adhesion to metal, fast curing, and fluoride release.

CRITICAL QUESTION

What is the setting mechanism of calcium aluminate glass-ionomer cement?

Calcium Aluminate Glass-Ionomer Cement

An innovative self-adhesive bioactive cement combines GIC with calcium aluminate cement. The unique cement is indicated for luting of fixed dental prostheses. The main ingredients in the powder are monocalcium aluminate, polyacrylic acid, tartaric acid, strontium-fluoro-alumino-glass, and strontium fluoride. The liquid component contains 99.6% water and 0.4% additives for controlling setting. The polyacrylic acid (PAA) functions as in a conventional GIC, crosslinked by Ca^{2+} ions from the soluble glass and the Ca-aluminate. The glass-ionomer reaction is responsible for setting time and strength. The working and setting time are reported to be 2 and 5 min, and the film thickness is low, $15 \pm 4 \mu\text{m}$. The resulting hydrated material is a composite of hydrated calcium aluminate cement and a crosslinked polyacrylate polymer. Setting expansion of 0.4% has been reported, although in vitro studies where the cement was set inside glass tubes did not show breakage. This amount of expansion was considered acceptable. The monocalcium aluminate absorbs water, which is reputed to impart bioactivity, forming hydroxyapatite at the margins of the cement and in contact with the pulp. A microstructural study showed the formation of hydroxyapatite over this cement in a phosphate buffer solution. The cement has long-term stability and strength for crown cementation. Results of a 3-year clinical study of 38 crowns and bridges revealed a favorable performance of this cement. The cement is packaged in powder–liquid systems for hand mixing or capsules using triturator.

CRITICAL QUESTION

What are the materials and techniques needed to overcome the root canal system environment and create a hermetic seal with endodontic obturation systems?

Endodontic Sealers

Endodontic sealers are specialized versions of dental cement (Figure 7-20) that are used during **obturation** with gutta-percha to fill voids and promote a close seal between the core and the dentinal walls of the canal, preventing or minimizing leakage, entombing residual microorganisms, and preferably filling areas of the root canal system that are inaccessible by instrumentation. The requirements for the ideal root canal sealer are listed in Box 7-1, and the ISO 6876 requirements are shown in Table 7-2. Several dental cements have been adapted for this specialized use; the most popular are ZOE-based sealers. ZOE sealers are inexpensive, are slow setting, and have a long history of acceptable clinical



• **Figure 7-19** Typical compomer materials. **A**, A powder–liquid system. **B**, Two single-paste systems. **C**, A paste–paste dual cartridge using static mixing. All systems are light-curable.



• **Figure 7-20** Root canal sealers. The two materials in the back are powder–liquid systems. The dual-cartridge syringe in the foreground is a paste–paste system with static mixing tip.

use. However, the newer epoxy-based sealers are radiopaque and more biocompatible than ZOE. Polyvinylsiloxane (PVS) sealers are also available as powder–liquid and two-paste systems. Glass-ionomer cement and resin-modified GICs have also been used. A filled biodegradable thermoplastic polymer, Resilon (Resilon Research LLC, Madison, CT), along with a resin-based sealer, Epiphany (Pentron Clinical Technologies, Wallingford, CT), was introduced in the 1990s. This system claimed to have less leakage than the traditional gutta-percha with sealer but performed poorly over time as a result of degradation of the polymer matrix. Another system uses gutta-percha cones that are coated with a proprietary resin coating (EndoREZ, Ultradent, South Jordan, UT) for use in combination with a methacrylate-based, dual-cured resin sealer and no dentin-bonding agent. In this case, the endodontic seal is dependent on the penetration of the hydrophilic sealer into the dentinal tubules and lateral canals following removal of the smear layer.

In the long, narrow space of the root canal, the application of any bonding system to form a uniform interface is challenging. For example, in bonding systems that contain volatile solvents, evaporation might be hindered. The canal anatomy is not only problematic to adhesive root canal obturation but also for the bonding of prefabricated posts. A further problem is that some irrigating solutions (e.g., sodium hypochlorite) and intracanal medicaments have adverse effects on root canal dentin collagen and the longevity of endodontic bonding. Unlike other cements, endodontic sealers are not light-cured because of the inability to complete the curing in the depths of a root canal (~2 cm), the complex anatomy of intercommunicating canals, and the inaccessible locations often in the posterior.

The configuration of the root canal also presents a high “C-factor” (Chapter 5, *Cure Shrinkage and Managing Shrinkage Stress*) because a nonbonded area of the cement layer exists within the bonded canal. Thus a resin endodontic sealer is subjected to severe stresses induced by the sealer’s polymerization shrinkage during setting. Debonding and gaps may occur between the sealer and dentin wall or in between the solid core material and the sealer along the periphery of the root canal obturation.

The newest category of endodontic sealers incorporates bioactive cements, such as Total Fill, Edge Endo, iRoot ES, and Endosequence BC Sealer. These materials are a single paste of tri-/dicalcium silicate powders suspended in organic liquids. Such

• BOX 7.1 Endodontic Sealer Criteria

Endodontic sealers should have the following characteristics:

- Make a hermetic seal
- Be tacky when mixed to provide good adhesion with the canal wall when set
- Contain particles of powder that are very fine so that they can mix easily with liquid, where appropriate
- Be radiopaque for visualization on a radiograph
- Not shrink upon setting
- Not discolor tooth structure
- Be bacteriostatic or at least not encourage bacterial growth
- Set slowly
- Be insoluble in tissue fluids
- Be well tolerated by the periapical tissue (and also not provoke an immune response, be mutagenic, or carcinogenic)
- Be soluble in common solvents, if necessary, to remove the root canal filling

sealers have a low setting expansion of 0.2% as a result of hydration-forming hydroxyapatite. Many sealers have shrinkage of 6% or higher, which leads to interface separation, whereas even a small expansion promotes hermetic interface sealing.

Resin-based sealers with bioactive fillers dispersed in the resin may not have the same bioactive effect as the single-paste sealer. The resins coat the bioactive particles and interfere with the release of calcium and hydroxide ions.

Tri-/Dicalcium Silicate Cement

Dental cements based on tri- and dicalcium silicates (*tricalcium silicate*, for short) are beneficial because of their sealing ability, biocompatibility, and bioactivity. These cements are less cytotoxic than glass-ionomer cements or polymeric materials. These **hydraulic cements** need water to set, which is ever present in the oral cavity. The first tri-/dicalcium silicate product was called *mineral trioxide aggregate* (MTA) and later, *bioceramic*. These names are widely used in dentistry to denote the tri-/dicalcium silicates products (Figure 7-21).

The essential components of these bioactive cements are tricalcium silicate and dicalcium silicate ceramic powders blended with inert radiopaque powders, usually bismuth oxide, zirconia, calcium tungstate, barium zirconate, or tantalum oxide. Minor phases of tricalcium aluminate, calcium sulfate (Table 7-10), calcium carbonate, and tetracalcium aluminoferrite are sometimes present, depending on the brand. The ferrite compound makes the cement gray.

Tricalcium silicate cement sets by reaction with water to form a rigid matrix of calcium silicate hydrates with embedded calcium hydroxide. The hydration starts on the surface of the tricalcium silicate particles and gradually penetrates inward, although never completely. Setting times for these products vary from a few minutes to 2 hours for the original ProRoot MTA. The long setting time, washout, and high price were major drawbacks of early products. Improved products are now available with shorter setting times based on finer particle sizes and modified water-based liquids containing calcium chloride, polycarboxylate, or various water-soluble organic materials.

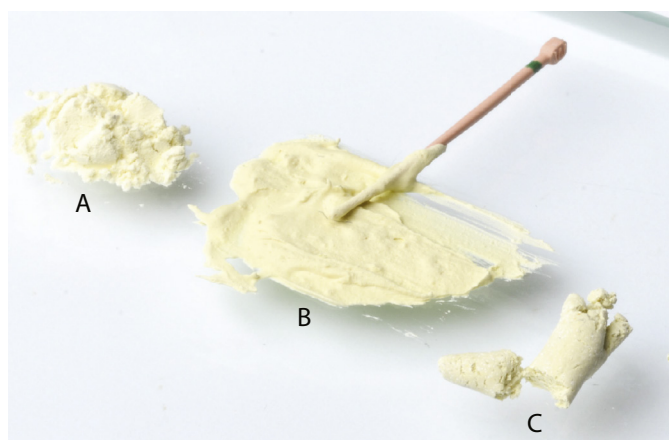
Products are available for a range of indications, from pulpal to periradicular contact. The primary indications are for pulp and periradicular tissue contact. The tri-/dicalcium silicate cements



• **Figure 7-21** An assortment of tricalcium silicate products with various packaging for the bioactive powder. **A**, Sachets. **B**, Bottles. **C**, Amalgam-type cartridges. **D**, Ampoules. **E**, Vials. **F**, Paste.

TABLE 7-10 Phases in Tricalcium Silicate Cement Before Hydration

Ceramic Phases	Wt%
Tricalcium silicate $3(\text{CaO})\cdot\text{SiO}_2$	45–75
Dicalcium silicate $2(\text{CaO})\cdot\text{SiO}_2$	7–32
Radiopaque filler (Bi_2O_3 , ZrO_2 , CaWO_4 , Ta_2O_5)	20–55
Minor phases, optional	
Tricalcium aluminate $3(\text{CaO})\cdot\text{Al}_2\text{O}_3$	0–13
Tetracalcium aluminoferrite $4(\text{CaO})\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	0–18
Gypsum $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	2–10
Calcium carbonate (CaCO_3)	<10



• **Figure 7-22** Mixing of mineral trioxide aggregate. **A**, Dispense powder and liquid. **B**, Bring the powder to liquid and spatulate until a putty-like consistency. **C**, Roll to the desired shape for usage.

are vulnerable to acid dissolution; therefore periodontal and coronal usage is only temporary. The cement sets over a wide range of P/L ratios, roughly between 4:1 and 2:1. The P/L ratio can be varied to suit the case and the clinician's preference. The powder should be dispensed onto a glass slab (Figure 7-22, A), with a drop of the liquid next to the powder. A medium-stiffness metal spatula should be used to bring powder to liquid and spatulate until a putty-like consistency is reached (Figure 7-22, B). The mixture can be formed into a "roll" with gloved fingers (Figure 7-22, C), and then the spatula can be used to cut off small sections for insertion into a pulpotomy preparation, a root-end filling of a perforation site, a cavity preparation, or a pulp exposure, such as a pulpotomy. A plastic filling instrument or a small amalgam carrier is commonly used to transport the cement into

the surgical location, and the cement is then gently compacted. If the mixed cement is not used immediately, a moist gauze "tent" can be placed over the material to prevent dehydration. If the mixture appears dry, usually more liquid can be added to prolong the working time.

The pH of MTA rises rapidly after contact with water by releasing calcium hydroxide as a reaction product. The calcium hydroxide in the set tricalcium silicate makes this material antibacterial, antifungal, and bioactive. That is, the high pH on the surface causes the precipitation of hydroxyapatite crystals on the surface in vitro or in vivo. MTA should not be allowed to stay in contact with the mucosa because the high pH can cause a superficial lesion. Excess material should be washed out of the oral cavity. The surficial layer of hydroxyapatite that forms in vivo causes a

chain of healing reactions to the bone-like surface, which does not appear as a foreign body to the cells. Reparative dentin forms in apposition to the tri-/dicalcium silicates in pulpal indications. Cementum-like layers form over the tricalcium silicate used to fill perforations, resorption defects, or root ends. When the tri-/dicalcium silicate materials set, the dimensional change is $< 0.1\%$ expansion, which is highly desirable for sealing, unlike polymers that shrink.

New bioactive, hydraulic paste products have been introduced. For these, the tri-/dicalcium silicate cement and radiopaque powders are suspended in organic liquids. When used in vivo, the organic liquid diffuses away from the powder, and water diffuses inward to cause setting. Such one-component paste products are being used for pulpal and periradicular containing cements, including endodontic sealing with gutta-percha.

Other hydraulic cements are likely to be developed that incorporate calcium monoaluminate to make a more acid-resistant cement suitable for infected (acidic) sights. Also, the reaction of silica hydrate (silicic acid) with calcium hydroxide (pozzolan reaction) will be used for new products to create a hydrated silica cement.

Calcium Phosphate Cements

Calcium phosphate cements are combinations of dicalcium phosphate dihydrate, dicalcium phosphate anhydrous, tricalcium phosphate, and tetracalcium phosphate that are mixed with an aqueous solution saturated with calcium phosphate, an organic acid, or a solution of polymers. An example is Sankin Apatite Root Canal Sealer (Dentsply Sankin, Tokyo, Japan).

The cement pastes gradually set and form hydroxyapatite. The calcium phosphate phases dissolve in the liquid and precipitate a less soluble calcium phosphate, which “sets” at 37°C , with some poorly crystalline hydroxyapatite being formed. The cements are suitable bone-substitute materials because they are gradually resorbed. They can sometimes be used in place of granular hydroxyapatite. However, their washout and low strength are problematic.

Experimental formulas of calcium phosphate base and liner products have been made that include polymerizable resins and additives in the liquid phase. The resins allow water diffusion that facilitates the conversion of calcium phosphate to hydroxyapatite. Clinical studies show that the caries-affected dentin underneath this cement had significantly more calcium and phosphorus content to a depth of $30\text{ }\mu\text{m}$, and the mineral content was in the range of healthy dentin after 3 months. Research continues to investigate such biocompatible materials for pulpal protection and endodontic indications.

Summary

No single cement is applicable for all indications in dentistry. Prudent dentists have several types of cements in their armamentarium. Manufacturers’ formulas and processes dictate most cement characteristics, but the clinician has some control over the handling, setting, and to some degree, the biocompatibility through the mixing ratios or technique.

The historic zinc phosphate cement has fallen out of use, but ZOE cements are used for luting, for temporary restorations, and for retaining fixed prostheses on implant-supported abutments,

which facilitates retrievability of the prostheses. Zinc polycarboxylate cements are noninjurious to the pulp and adhesive to tooth structure, but they are not commonly used because of their short working time and viscous nature.

Glass-ionomer cements work well for orthodontic bands and cementing of metal crowns on primary teeth. The fluoride-releasing capability makes glass-ionomer cement the material of choice for the replacement of restorations that have failed because of recurrent caries and for patients living in areas where fluoridated drinking water is not available. A primary disadvantage of glass-ionomer cements is the slow maturing process that is required to develop their highest strength.

Resin cements are insoluble in oral fluids, and their fracture toughness is higher than that of other cements. Resin cements can be used for all types of cementation, most notably for prostheses with poor retention, and for all-ceramic prostheses where the esthetic demand is very high. Resin cements require bonding agents to be effective. Etching may be required to obtain a strong attachment to enamel with bonding agents. Self-etching and self-adhesive resin cements are now available.

Hybrid ionomer cements are used as a liner, fissure sealant, and base material and in core buildups and orthodontic band cementation. Compomers are used for cementing metallic prostheses and some restorative indications. The durability of compomers is inferior to that of resin-based composites; thus they should only be used for low-stress areas.

Glass-ionomer, polycarboxylate, and resin cements adhere chemically and physically to the surrounding surfaces. Excess cement should be removed as soon as the seating is completed to prevent adhesion to the exterior of the prostheses or surrounding teeth. A separating medium, such as petroleum jelly, spread on external and surrounding surfaces inhibits cement adherence, making cement removal easier when these cements fully set.

The important properties of cements for adhering devices are summarized in Table 7-11. A high elastic modulus was important for gold alloy restorations, and a lower elastic modulus is needed under ceramic restorations.

Pulp capping and cavity liners/base materials are important for pulpal health and protection from acidic cements. GICs elicit a greater pulpal reaction than ZOE cement but less than zinc phosphate cement. Calcium hydroxide and tricalcium silicate products are important for direct or indirect pulpal protection. These bioactive materials initiate subgingival or pulpal tissue healing, although the tricalcium silicates are superseding calcium hydroxide products, especially for pulpotomies.

Calcium aluminate–glass-ionomer cement relies on the GIC to establish the early strength and the hydration of calcium aluminate for final properties and bioactivity. New formulas of cements are anticipated, based on calcium aluminates and pozzolanic cements. The latter cement is based on silicic acid reacting with calcium hydroxide, often called *Roman cement*.

Specialty areas of dentistry, such as orthodontics and endodontics, use variations of the cements discussed to achieve the unique needs for their procedures. Endodontic cement formulas include ZOE, epoxy, polyvinyl siloxane, and now the tricalcium silicates. The tricalcium silicates are used surgically and nonsurgically, depending on the viscosity of the cement used.

Cements for dentistry continue to evolve and improve in their insolubility, sealing, esthetics, bonding, and durability. Filler particles, usually glass, continue to move to smaller sizes. *Nanoparticles* is now a commonly used term, which usually means silica particles are included, but the material may include other

TABLE 7-11 Properties of Cements for Affixing Devices

Cement Type	Setting Time (min)	Film Thickness (μm)	24-h Compressive Strength (MPa)	24-h Diametral Tensile Strength (MPa)	Elastic Modulus (GPa)	Solubility in Water (wt%)
Zinc phosphate	5.5	20	104	5.5	13.5	0.06
ZOE* (type I)	4.0–10	25	6–28	—	—	0.04
ZOE–EBA (type II)	9.5	25	55	4.1	5.0	0.05
ZOE + polymer (type II)	6.0–10	32	48	4.1	2.5	0.08
Zinc polycarboxylate	6.0	21	55	6.2	5.1	0.06
Glass ionomer	7.0	24	86	6.2	7.3	1.25
Resin	2.0–4.0	<25	70–172	—	2.1–3.1	0–0.01

EBA, ethoxybenzoic acid; ZOE, zinc oxide–eugenol.

fillers that have some portion of particles finer than 0.1 μm (100 nm). New adhesive polymers and refinement of the fillers will continue to help dentists minimize tissue destruction and maximize preservation.

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Acknowledgment

Figure 7-2 was generously provided by Dr. Carlos Alberto de Souza Costa of São Paulo State University, Brazil.

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Dental Amalgams

OUTLINE

Amalgam Alloy

Clinical Manipulation of Amalgam for Restorations

Properties of Amalgams

Clinical Performance of Amalgam Restorations

Safety of Amalgam Restorations

KEY TERMS

Amalgam An alloy containing mercury.

Amalgamation The process of mixing liquid mercury with one or more metals or alloys to form an amalgam.

Condensation The process of pressing dental amalgam by force to remove excess mercury and ensure continuity of the matrix phase.

Creep The time-dependent strain or deformation that is produced by a stress. The creep process can cause an amalgam restoration to extend out of the restoration site, thereby increasing its susceptibility to marginal breakdown.

Delayed expansion The gradual expansion of a zinc-containing amalgam over a period of weeks to months. This expansion is associated with the development of hydrogen gas, which is caused by the incorporation of moisture in the plastic mass during its manipulation in a cavity preparation.

Dental amalgam An alloy that is formed by reacting mercury with silver, copper, and tin, and that may also contain palladium, zinc, and other elements to improve handling characteristics and clinical performance.

Dental amalgam alloy (alloy for dental amalgam) An alloy of silver, copper, tin, and other elements that is processed in the form of powder particles or as a compressed pellet.

Marginal breakdown The gradual fracture of the perimeter or margin of a dental amalgam filling, which leads to the formation of gaps between the amalgam and the tooth.

Trituration The mixing of amalgam alloy particles with mercury in a device called a *triturator*; the term is also used to describe the reduction of a solid to fine particles by grinding or friction.

When metal particles are mixed with mercury in certain proportion at room temperature, the mixture appears plastic initially. At that consistency, the mixture can be adapted to any shape with light pressure. Meanwhile, the outer portion of the particle in the mixture dissolves into mercury that slowly hardens the mixture. When the solubility of the metal in mercury is exceeded, crystals of mercury-containing compounds start to precipitate within the mercury. The process increases the firmness of the mixture, which enables sculpting of the mixture to the desirable anatomical form with instruments. The reaction continues at a slower rate as the mixture transforms into a solid with sufficient strength to resist fracture. The reaction process is called **amalgamation**, and the metallic solid containing mercury is called **amalgam**.

CRITICAL QUESTION

After reacting with liquid mercury, how do the original powder particles become structural components of the set dental amalgams?

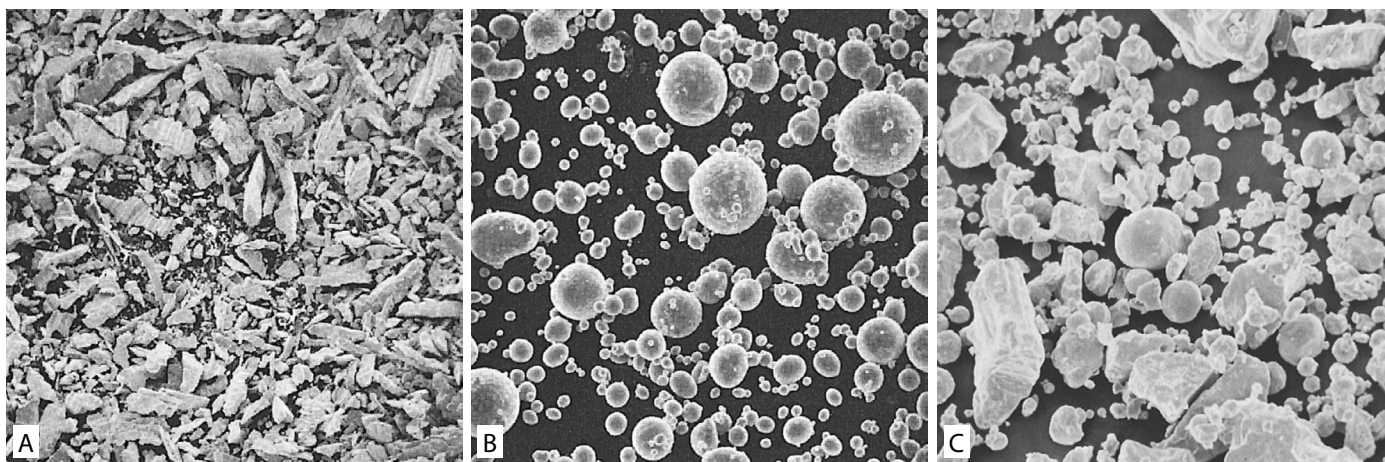
Amalgam Alloy

The amalgams used today are largely based on the formulation published by G. V. Black in 1895. The major modifications to that formulation were raising the copper content and the making

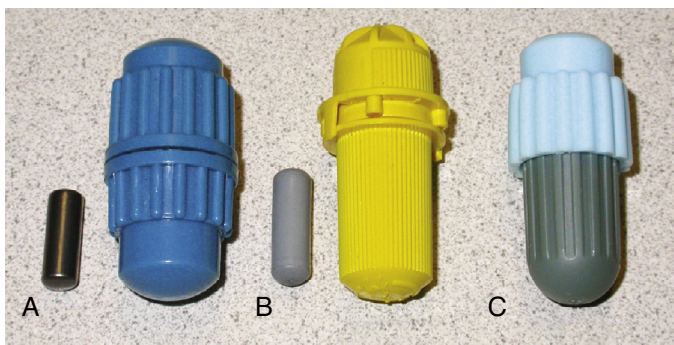
of spherical particles during the early 1960s. Despite amalgam's long history of success as a restorative material, there have been periodic concerns regarding the potential adverse health effects arising from exposure to mercury in **dental amalgam**. Because of advances in resin-based composites and adhesive technology in dentistry, the use of amalgam has declined substantially. Dental amalgam use will be limited in the future and may eventually be phased out of the clinician's armamentarium.

As with other materials discussed in this book, practical skill and sound scientific familiarity with the material are needed for making high-quality restorations. Even when no new amalgams are being placed in patients, there will still be billions of amalgam restorations remaining in patients' mouths. Many of these restorations will require attention, such as for replacement, repair, or refurbishing procedures. In this chapter, amalgam structure, properties, and manipulation characteristics are discussed. However, these concepts require an understanding of several key terms commonly used by the dental profession.

Before these alloys combine with mercury, they are known as **dental amalgam alloys**. They are usually provided as (1) irregularly shaped particles (**Figure 8-1, A**) produced by milling or lathe-cutting a cast ingot of the amalgam alloy, (2) as spherical particles (**Figure 8-1, B**) produced by atomizing the liquid alloy in a chamber filled with inert gas, or (3) as a mixture of both lathe-cut and



• **Figure 8-1** Particle shapes of dental amalgam alloys. **A**, Conventional lathe-cut alloy ($\times 100$). **B**, Spherical alloy ($\times 500$). **C**, Typical admix high-copper alloy powder showing the lathe-cut silver-tin particles and silver-copper spherical particles ($\times 500$).



• **Figure 8-2** Types of amalgam trituration capsules. **A**, Reusable capsules with pestle. **B**, Preproportioned capsule with pestle. **C**, Preproportioned capsule without pestle.

spherical particles (Figure 8-1, C). The powder may also be compacted in the form of pellets, which are readily crushed to powder during **trituration**, the process of mixing mercury and alloy.

Originally, the dentist had to dispense alloy powder and mercury in a mortar and mix them together with a pestle by hand. Later, the components were dispensed in a reusable capsule (Figure 8-2) with a pestle and triturated by a power-driven mechanical device called a **triturator** (Figure 8-3). Today, disposable amalgam capsules are widely available. Each capsule contains a predetermined amount of alloy powder and mercury in a sealed pouch, and the capsule is sealed to prevent evaporation of the mercury.

Composition

Amalgam alloys are classified as either a low-copper (conventional) or high-copper alloy (Table 8-1). In both types, the major components of the alloys are silver and tin.

The Silver-Tin System

Figure 8-4 is an equilibrium-phase diagram of the silver-tin alloy system. Conventionally, starting from the left of the phase diagram, each phase is designated in Greek alphabetical order. The ratio of silver to tin in Table 8-1 shows that amalgam alloys have a narrow range of compositions, falling within the $\beta + \gamma$ and the γ phases of the diagram.



• **Figure 8-3** A programmable triturator.

TABLE 8-1 Composition of Some Typical Commercial Amalgam Alloys

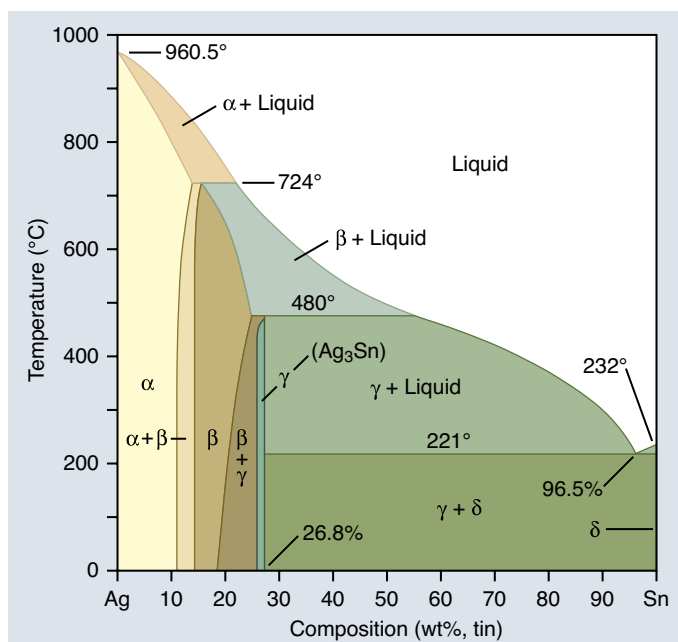
Amalgam	COMPOSITION (MASS %)			
	Ag	Sn	Cu	Zn
Low copper (lathe-cut)	70.3	25.9	2.8	0.9
Low copper (spherical)	72.0	25.0	3.0	—
High copper (admix)	69.5	17.7	11.8	1.0
High copper (spherical)	61.0	26.0	13.0	—

CRITICAL QUESTION

How can zinc be a beneficial additive to alloy for dental amalgam but also a component that can potentially cause significant postoperative discomfort to the patient?

Low-Copper Alloys

Silver-tin alloys are quite brittle and difficult to blend uniformly unless a small amount of copper is substituted for silver. The chief function of zinc in an amalgam alloy is to act as a



• **Figure 8-4** Equilibrium-phase diagram of silver-tin system.

deoxidizer that reacts with oxygen during melting to minimize the oxide formation of other constituents. Alloys without zinc are more brittle, and their amalgams tend to be less plastic during **condensation** and carving. The specification of the American Dental Association (ADA) for amalgam alloys allows some mercury in the alloy powder. The structure of these conventional alloys was dominated by Ag_3Sn (γ phase), with some Cu_3Sn (ϵ phase).

High-Copper Alloys

The first high-copper alloy was formulated by mixing one part of silver-copper eutectic spherical spheres particles with two parts lathe-cut particles of Ag_3Sn . This modification raises the copper content to 11.8% by weight. This is often called *dispersed-phase alloy* or *admixed high-copper alloy*. A second type of high-copper alloy was made by melting all components of the dispersed-phase alloy. This process yields a single composition system. The presence of the higher copper content makes cutting the powder into particles difficult. Thus they are often provided in a spherical form that is produced by an atomization process. The copper content of this group of alloys could be as high as 30% by weight. Various amounts of indium or palladium have been included in some commercial systems.

Gallium-Based Alloys

Gallium, when alloyed with indium or tin, can be a liquid at room temperature. It has been used to triturate with alloys for high-copper amalgam as a substitute for mercury.

Powder Configuration

Dental amalgams are made by mixing alloy powders with mercury. The reaction begins at the particle–mercury interface. Therefore the physical configuration and condition of the particles have a significant influence on the setting process.

Lathe-Cut Powder

An as-cast ingot is first annealed to retain a uniform phase, and then placed in a milling machine or in a lathe to be fragmented by a cutting tool or bit. The powders obtained from cutting are acid-washed to produce a more reactive surface. Because the stresses induced into the particle during cutting are not uniform and can slowly be self-relieved over time, they can cause the performance of the amalgam to be inconsistent.

Atomized Powder

The molten amalgam alloy is atomized into fine spherical droplets of metal in a chamber of inert gas. If the droplets solidify before hitting a surface, the spherical shape is preserved, and these atomized powders are called *spherical powders*. Like the lathe-cut powders, spherical powders are given an annealing heat treatment and surface washing. Note in [Table 8-1](#) that alloys for making spheres do not contain zinc because there is no oxygen in the chamber to cause oxidation.

Particle Size

The average particle sizes of modern powders range between 15 and 35 μm . Smaller particles greatly increase the surface area per unit volume of the powder. A powder containing tiny particles requires a greater amount of mercury to form an acceptable amalgam. The particle-size distribution can affect the character of the finished surface. When the amalgam has partially hardened, the tooth anatomy is carved in the amalgam with a sharp instrument. During carving, the larger particles may be pulled out of the matrix, producing a rough surface. Such a surface is probably more susceptible to corrosion than a smooth surface. A smaller average particle size tends to produce a more rapid hardening of the amalgam, with greater early strength.

Lathe-Cut Powder Versus Spherical Powder

Amalgams made from lathe-cut powders or admixed powders tend to resist condensation better than amalgams made entirely from spherical powders. Because freshly triturated amalgams from spherical powders are very plastic, one cannot rely on the pressure of condensation to establish the proximal contour for a class II restoration. Spherical alloys require less mercury than typical lathe-cut alloys because spherical alloy powder has a smaller surface area per volume than does the lathe-cut powder. Amalgams with low mercury content generally have better mechanical properties.

CRITICAL QUESTION

Through what mechanism does the addition of 6 wt% or more of copper by weight prevent the formation of the undesirable γ_2 phase?

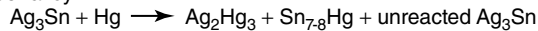
Amalgamation

As discussed earlier, modern dental amalgam alloys are based on the intermetallic compound Ag_3Sn ; therefore the main reaction occurring after trituration with mercury will mainly be that between Ag_3Sn and mercury. Other elements in the alloy, especially copper, also play a significant role in the final microstructures of set amalgams.

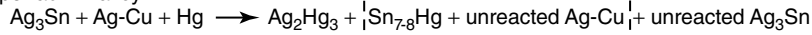
Low-Copper Alloys

The main reaction products of low-copper alloy are the body-centered cubic Ag_2Hg_3 (γ_1) phase and the hexagonal Sn_{7-8}Hg (γ_2) phase ([Figure 8-5](#)). Both phases are designated γ because they happen to be the third phase of the respective Ag–Hg and Sn–Hg

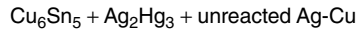
Low-copper alloy



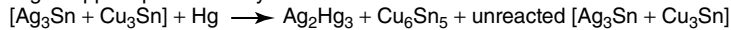
High-copper admix alloy



Secondary
solid-state reaction



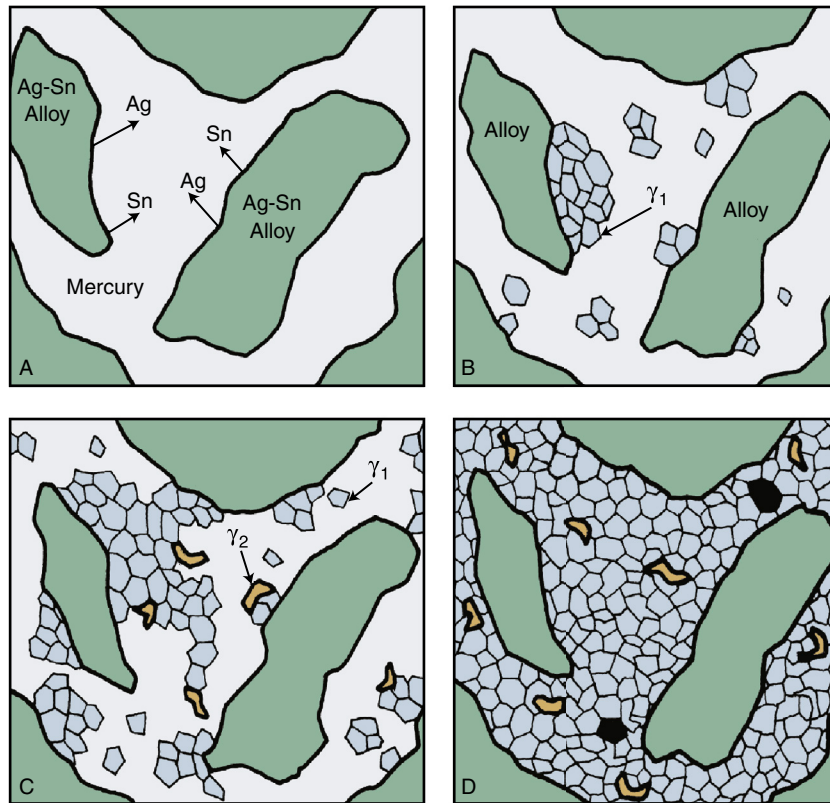
High-copper spherical alloy



Symbols and stoichiometry of phases

Phase Symbols	Composition
γ	Ag_3Sn
γ_1	Ag_2Hg_3
γ_2	Sn_{7-8}Hg
ϵ	Cu_3Sn
η (η')	Cu_6Sn_5

• **Figure 8-5** Reactions of low-copper and high-copper amalgams and symbols of phases involved in the setting of dental amalgams.



• **Figure 8-6** Schematic drawings that illustrate the development sequence of the amalgam microstructure when lathe-cut, low-copper, alloy particles are mixed with mercury. **A**, Dissolution of silver and tin into mercury. **B**, Precipitation of γ_1 crystals in the mercury. **C**, Consumption of the remaining mercury by growth of γ_1 and γ_2 grains. **D**, The final set amalgam. The dark patches are voids.

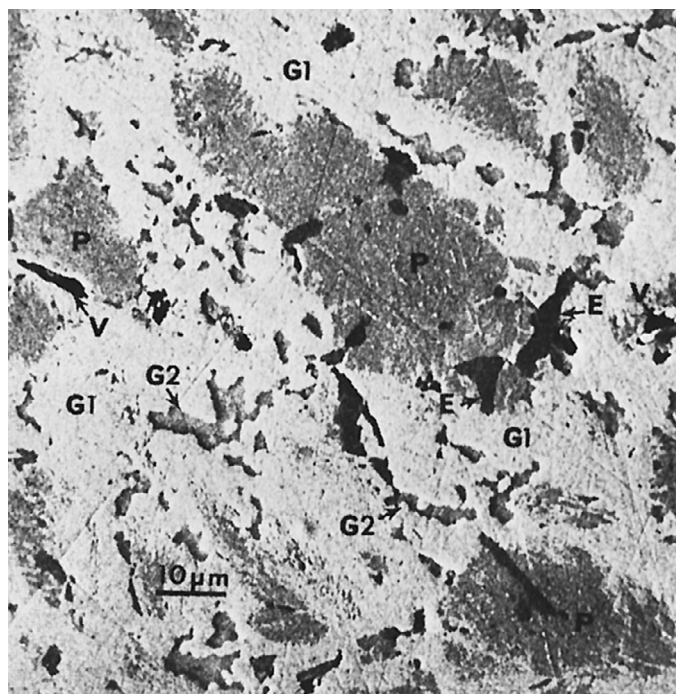
systems. Because the solubility of silver in mercury is much lower than that of tin, the Ag_2Hg_3 phase precipitates first and is designated as γ_1 , whereas the Sn_{7-8}Hg phase precipitates later and is designated as γ_2 . There is evidence from x-ray diffraction and thermal analyses of set amalgam that a δ phase, which is richer in mercury than γ_2 , is present in low-copper alloy instead of γ_2 . The existence of γ_2 or δ phases in low-copper amalgams remains an unresolved question. For the purpose of this discussion, the Sn-Hg phase is designated as γ_2 .

The low-copper alloy is usually mixed with mercury in about a 1:1 ratio. This amount of mercury is insufficient to consume the alloy particles completely; consequently, unreacted particles are present in the set amalgam. Thus a typical low-copper amalgam is a composite in which the unreacted particles are distributed within the γ_1 and γ_2 phases. The sequence of amalgamation of the silver-tin alloy is shown schematically in Figure 8-6.

The physical properties of the set amalgam depend on the relative percentages of each microstructural phase. The greater the number of unreacted Ag-Sn particles retained in the final structure, the stronger the amalgam will be. The γ_2 phase is the weakest and least stable in a corrosive environment and may suffer corrosion attack, especially in the crevices of the restorations. A reaction between Cu_3Sn (ϵ phase) and γ_2 also occurs and yields Cu_6Sn_5 (η' phase) to a lesser extent because of the low copper content. Figure 8-7 illustrates the features found in a typical microstructure of amalgam made from a lathe-cut, low-copper alloy.

CRITICAL QUESTION

Compared with amalgams made from admixed high-copper alloys, what are the benefits and the risks of the amalgams made from high-copper, single-composition, spherical particles?



• **Figure 8-7** A scanning electron micrograph of a low-copper amalgam ($\times 1000$). The micrograph features remaining β and γ phases (the large, dark areas labeled P), ϵ phase (small, dark patches labeled E), γ_1 phase (light background labeled $G1$), γ_2 phase (small grains labeled $G2$), and voids (left-center and right-center areas labeled V).

High-Copper Alloys

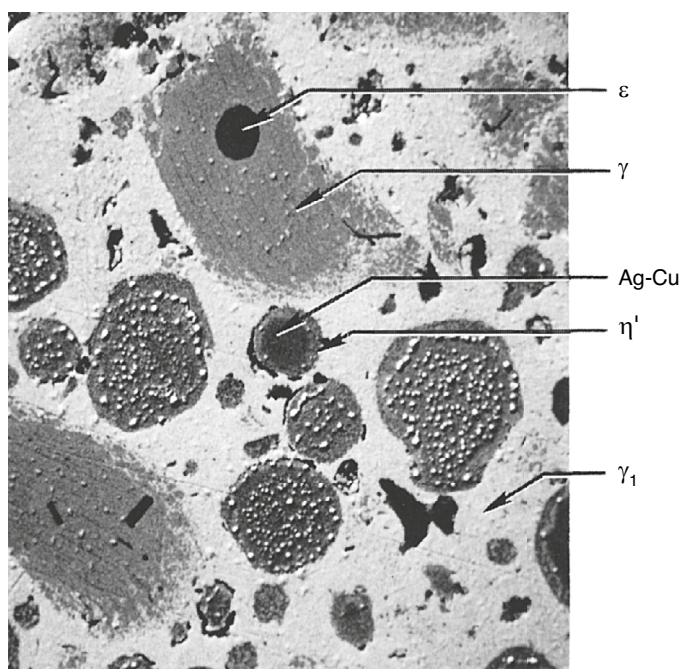
As discussed earlier, high-copper alloy powders are available in a two-phase admixed powder and a single-composition, single-phase powder, each with a unique amalgamation process (Figure 8-5).

Admixed Alloys

When mercury mixes with an admixed alloy powder, the silver in the Ag-Cu spheres and the silver and tin from Ag-Sn particles dissolve into the mercury. Although both γ_1 and γ_2 crystals form, as in lathe-cut alloys, the tin in mercury diffuses to the surfaces of the Ag-Cu alloy particles and reacts with the copper to form a layer of η' -phase crystals on the surface. The η' layer on the surface of Ag-Cu alloy particles also contains γ_1 crystals because the γ_1 and η' phases form simultaneously. In this reaction, the γ_2 phase forms along with the η' phase, but the γ_2 phase later reacts with copper from Ag-Cu spheres, yielding additional η' phase (the secondary solid-state reaction in Figure 8-5). The γ_2 phase can be eliminated with at least 12% of copper by weight in the alloy powder. Figure 8-8 illustrates the microstructure of an admixed amalgam. As in the low-copper amalgams, admixed amalgam is a composite of γ_1 because of the matrix phase with discrete unreacted alloy particles.

Single-Composition Alloys

The major components of single-composition particles are usually silver, tin, and copper. The copper content of various single-composition alloys ranges from 13% to 30% by weight. Some alloys contain a small quantity of indium or palladium. Several phases are found in each single-composition alloy particle, including the β phase (Ag-Sn), γ phase (Ag₃Sn), and ϵ phase (Cu₃Sn). Some of the alloys may also contain the η' phase. The particles usually



• **Figure 8-8** Scanning electron micrograph of an admixed high-copper amalgam. The various phases and reaction layer are labeled. The ϵ phase is part of the lathe-cut particle. The small, very light, drop-shaped areas on the particle phase are high in mercury because of the freshly polished specimen ($\times 1000$).

are spheres, but a formulation with all lathe-cut particles is also available.

When triturated with mercury, silver and tin from the Ag-Sn phases dissolve in mercury. Very little copper dissolves in mercury. The γ_1 crystals grow, forming a matrix that binds together the partially dissolved alloy particles. The η' crystals are found as meshes of rod-like crystals at the surfaces of alloy particles dispersed in the matrix. In most single-composition amalgams, little or no γ_2 forms (see Figure 8-5). Figure 8-9 shows the microstructure of a typical single-composition amalgam. This structure includes unreacted alloy particles, γ_1 grains, and η' crystals.

CRITICAL QUESTION

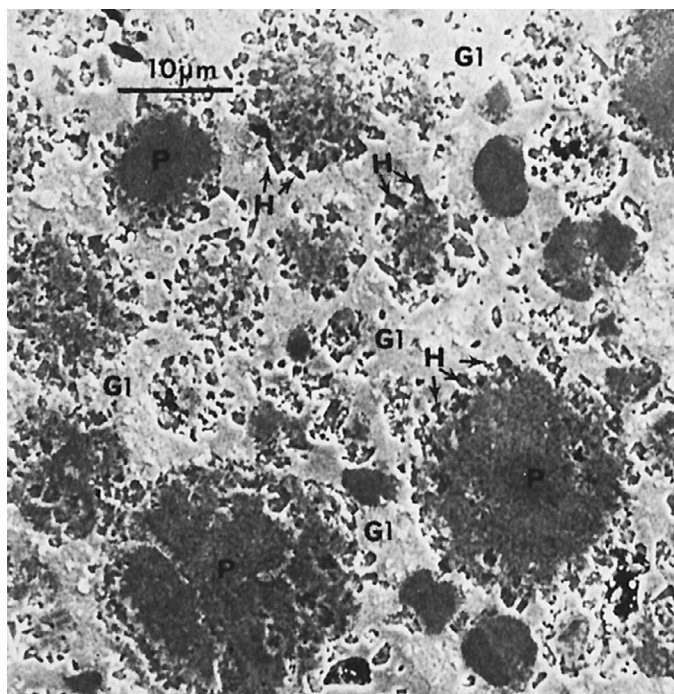
What steps can be taken by a dentist to extend the survival time of amalgam restorations?

Clinical Manipulation of Amalgam for Restorations

A good modern dental amalgam alloy can be manipulated so that the restoration lasts, on average, 12 to 15 years. The cavity preparation must be designed correctly, and the amalgam must be manipulated properly so that no part of the amalgam restoration is placed under excessive tensile stress. The manipulation variables discussed in this section are the mercury/alloy ratio, trituration, and condensation.

CRITICAL QUESTIONS

What is the ideal mercury/alloy ratio for an admixed amalgam and a spherical particle amalgam? What are the consequences of insufficient and excess amounts of mercury for the amalgam restorations?



• **Figure 8-9** A scanning electron micrograph of a high-copper, single-composition amalgam ($\times 560$). The micrograph features unreacted alloy particles (labeled *P*), γ_1 matrix phase (labeled *G1*), and η' crystals (labeled *H*).

Mercury/Alloy Ratio

The mercury/alloy ratio is the weight of mercury divided by the weight of alloy needed for trituration. Sufficient mercury must be present in the original mix to provide a coherent and plastic mass after trituration, but the amount must be low enough that the mercury content of the restoration is at an acceptable level without the need to remove an appreciable amount during condensation. The mercury content of the lathe-cut alloy is about 50% by weight, and that for spherical alloys is 42% by weight. When a mortar and pestle were used for mixing amalgam, an excess amount of mercury would be needed to achieve a smooth and plastic amalgam. Removal of excess mercury would be accomplished by squeezing or wringing the mixed amalgam in a squeeze cloth prior to insertion of the increments into the prepared cavity.

The most common dispenser is based on volumetric proportioning. Preweighed pellets or tablets are first placed in a capsule (Figure 8-2). In mechanical mixing, the capsule serves as a mortar. The mercury dispenser should be held vertically to ensure consistent dispensing of mercury. The dispenser should always be at least half full when used to ensure that the proper weight of mercury is dispensed.

Disposable capsules containing preproportioned mercury and alloy are now widely used. Both components are physically separated in the capsule. Some capsule designs require activation before trituration to bring the components together. Other designs, called *self-activating capsules*, bring the alloy and mercury together automatically during the first few oscillations of the amalgamator.

Regardless of the method used, the proper amount of mercury and alloy must always be proportioned, or the preproportioned capsule must be activated just before the start of trituration.

CRITICAL QUESTION

How should the optimal trituration time be determined for a given dental amalgam product?

Mechanical Trituration

The objective of trituration is to ensure proper amalgamation of the mercury and alloy and provide the optimal consistency for condensation. The focus of trituration includes the triturator and the consistency of the mixture.

Tritrators

The main mixing mechanism of a triturator is a reciprocating arm holding the capsule under a protective hood. The hood is to confine mercury that might escape into the room and to prevent a capsule from being accidentally ejected from the amalgamator during trituration. Older models are usually a single-speed device with an automatic timer to set the length of mixing. Later models have multiple speed settings. A modern triturator is often micro-processor controlled (Figure 8-3) and contains preset trituration programs for several materials. These newer models can also be programmed by the operator to include other materials. The capsule serves as a mortar. A cylindrical metal or plastic piston of smaller diameter than the capsule is inserted into the capsule, and this serves as the pestle. Spherical alloys often do not need a pestle (Figure 8-2).

Alloy manufacturers often provide a list of recommended time schedules and speed settings in cycles per minute for their alloys and various types of amalgamators. Because of the speed variations in amalgamators, the schedule should serve only as a rough guide. Dentists and assistants may want to adjust the time required to attain a mix of the correct consistency. For a given alloy and mercury/alloy ratio, increased trituration time and/or speed shorten the working and setting times.

A reusable capsule should be clean and free of previously mixed, hardened alloy. At the end of each trituration procedure, one should quickly remove the pestle from the capsule, replace the lid, reinsert the capsule in the amalgamator, turn it on for a second or two, and then remove the amalgam. This mulling process generally causes the mix to cohere so that the amalgam can be readily removed from the capsule with minimal residue in the capsule. Mulling minimizes the need for scraping out partially hardened alloy, which usually produces scratches in the capsule.

Consistency of the Mix

The proper time of mixing can be determined by observing the consistency of the mix. For example, the mix with a somewhat grainy and dull appearance (Figure 8-10, *A*) indicates undertrituration. Not only will the amalgam restoration made from this mix be weak, but also the rough surface left after carving of the granular amalgam will increase the susceptibility to tarnish. If the trituration has produced an amalgam of the general appearance shown in Figure 8-10, *B*, the strength will be optimal, and the smooth carved surface will retain surface luster longer after polishing. Because of the friction between particles during trituration, such an amalgam mix should be warm (not hot) when the mix is removed from the capsule. This will have no effect on the physical properties of the amalgam other than to shorten the working time somewhat. Overtrituration through a higher speed or a longer mixing time results in a softer (mushy) mixture that often sticks to the wall of the capsule. Compared with the properly mixed



• **Figure 8-10** Appearance of freshly triturated amalgam mixture. **A**, A grainy, undertriturated mixture; a restoration made of such a mixture has low strength and poor resistance to corrosion. The mixture may appear as a solid mass, but the surface remains without luster, as shown. **B**, A properly triturated amalgam that appears rounded, with a smooth, shiny surface. **C**, An overtriturated amalgam mixture, which is shinier than that of the properly triturated one, and because of more fluid consistency, the mass appears flattened by the force of trituration.

amalgam, the surface of overtriturated amalgam is shinier, the shape of the mass is flatter (Figure 8-10, C), and the working time is shorter and has a slightly higher setting contraction.

CRITICAL QUESTION

During the condensation of an amalgam, at what point in time should the triturated mixture be discarded and replaced by a new mixture?

Condensation

The goal of condensation is to compact the alloy into the prepared cavity so that the greatest possible density is attained, with sufficient mercury present to ensure continuity of the matrix phase between the remaining alloy particles. This results from a reduction of excess mercury and porosity within the set amalgam.

After the mix is made, the increments of alloy should be carried to, and inserted in, the prepared cavity by means of instruments such as small forceps or an amalgam carrier designed for this purpose. Condensation of the amalgam should then be promptly initiated. The field of operation must be kept absolutely dry during condensation. Because of the nature of the operation, condensation is usually accomplished within four walls and a floor. One or more walls may be a thin sheet of stainless steel, called a *matrix band*.

Condensation Procedure

Condensation is pressing a condenser point on the amalgam mass under hand pressure. This procedure is usually started at the center, and then the condenser point is stepped incrementally toward the cavity walls. The force requirements depend on the shape of the alloy particle.

After condensation of an increment, the surface should appear shiny. This indicates that there is sufficient mercury present at the surface to diffuse into the next increment so that the subsequent increment added will bond to the preceding one. Removing some of the soft or mushy material before adding the next increment is desirable. This step is less critical with modern-day amalgams that require less mercury for mixing.

If the cavity is a large one or if for some reason undue time is taken to complete condensation, another mix should

be made just before the original one is used up or when plasticity is lost. Condensation of partially set material fractures and breaks up the matrix that has already formed. In addition, when the alloy has lost a certain amount of plasticity, condensation without producing internal voids and layering is difficult. The procedure of condensation is continued until the cavity is overfilled.

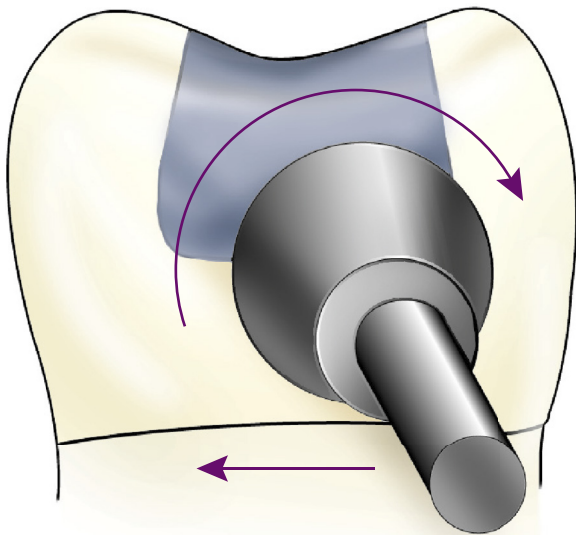
Condensation Pressure

The condensation pressure is governed by the area of the condenser face and the force exerted by the operator on the mixture. When a given force is applied, the smaller the condenser, the greater is the pressure exerted on the amalgam. If the condenser point is too large, the operator cannot generate sufficient pressure to condense the amalgam adequately and force the mix into retentive areas. A study of 30 practitioners showed that the forces applied are in the range of 13.3 to 17.8 N (3 to 4 lb). To ensure maximum density and adaptation to the cavity walls, the condensation force should be as great as the alloy will allow, consistent with patient comfort. Many of the spherical alloys offer only minimal resistance to the condensation force. Therefore the strength properties of spherical amalgam alloys tend to be less sensitive to condensation pressure.

In many instances, condensation becomes a matter of attaining good adaptation. The potential disadvantages of a spherical alloy compared with an admixed alloy (lathe-cut and spherical particles) are the tendency for overhangs in proximal areas and weak proximal contacts. The shape of the condenser points should conform to the area under condensation. For example, a round condenser point is ineffective adjacent to a corner or angle of a prepared cavity; a triangular or square point is indicated in such an area. Points of various shapes are available to provide effective condensation.

Carving and Finishing

After the amalgam has been condensed into the prepared cavity, it is carved to reproduce the proper tooth anatomy. The objective of carving is to simulate the anatomy rather than trying to reproduce extremely fine details. The carving should start only when the amalgam is hard enough to resist the carving instrument. A scraping or “ringing” sound should be heard when the amalgam



• **Figure 8-11** Final finishing of an amalgam margin with a soft, unribbed prophylaxis cup and fine prophylaxis paste. The cup should be used with very light pressure to avoid flattening of anatomical contours.

is carved. Softer amalgam may be pulled away from the margins by the carving instrument. The matrix band should be removed during the final carving procedure. Make sure that excess amalgam has not been forced beyond the matrix gingivally during condensation.

After carving, the surface of the restoration should be smoothed. This may be accomplished by burnishing the occlusal surface with a ball burnisher and the margins of the restoration with a rigid, flat-bladed instrument. Final smoothing can be concluded by rubbing the surface with a moist cotton pellet or by lightly smoothing the surface with a rubber polishing cup and an extremely fine polishing or prophylaxis paste (Figure 8-11). Clinical data on the performance of restorations support the desirability of burnishing the fast-setting, high-copper systems. Burnishing slow-setting alloys can damage the margins of the restoration.

Regardless of alloy, trituration method, or condensation technique, the carved surface of the restoration appears rough, as demonstrated by the dull surface of the restorations shown in Figure 8-12, *A*. The surfaces are covered with scratches, pits, and irregularities, which can result in concentration cell corrosion over time (Chapter 3, Concentration Cell Corrosion). The smooth surface on the restorations shown in Figure 8-12, *B* is produced by the final finishing procedure. The final finish of the restoration should be delayed for at least 24 hours after condensation and preferably longer. Further discussion on polishing amalgams can be found in Chapter 16, Dental Amalgams.

Properties of Amalgams

ADA Specification No. 1 (International Organization for Standardization [ISO] 24234) for amalgam alloys lists dimensional change, compressive strength, and **creep** as the measures of amalgam quality. The controlling variables and significance of these properties are described later.

CRITICAL QUESTION

How does the mercury content and condensation method affect the expansion or contraction that may occur during the setting of an amalgam restoration?



• **Figure 8-12** Effect of amalgam polishing. *A*, Amalgam restorations as they appear after carving. *B*, The same restorations after final finishing. (Courtesy Dr. Saulo Geraldelli.)

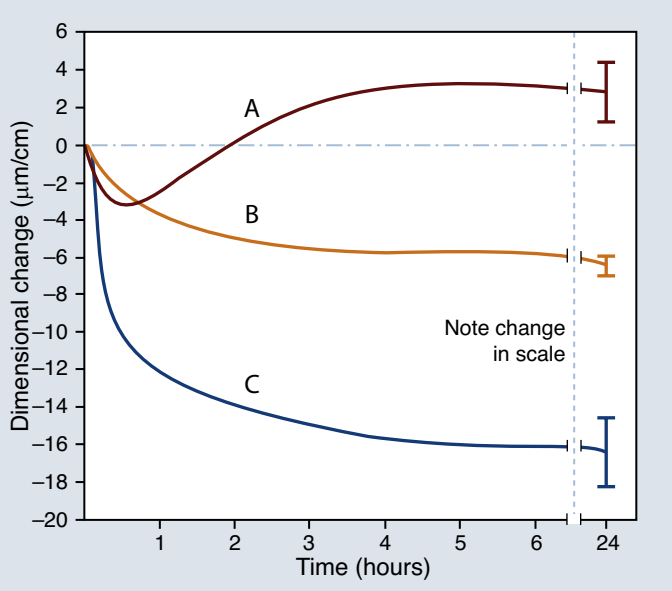
Dimensional Stability

Amalgam contracts or expands as the material sets. Severe contraction can lead to microleakage, plaque accumulation, and secondary caries. Excessive expansion can produce pressure on the pulp and postoperative sensitivity. Protrusion of a restoration can also result from excessive expansion. ADA Specification No. 1 states that the dimensional change of amalgam should be in the range of 15 to 20 $\mu\text{m}/\text{cm}$ measured at 37 °C between 5 minutes and 24 hours after the beginning of trituration.

Mechanism of Dimensional Change During Setting

When the alloy and mercury are mixed, contraction results as the particles dissolve. Because the final volume of the γ_1 phase is less than the sum of the silver and liquid mercury volume needed to produce the γ_1 phase, contraction continues as the γ_1 phase keeps forming. In time, the γ_1 crystals begin impinging against one another, causing expansion when there is enough liquid mercury making the matrix phase plastic. When the matrix phase becomes rigid, further impingement of γ_1 crystals cannot force the matrix to expand further. The reaction continues with γ_1 crystals growing into interstices containing mercury.

This model implies that greater expansion will occur if sufficient mercury is present in the mix when the dimensional change begins. Therefore mixtures with less mercury in the mix, as for lower mercury/alloy ratios and higher condensation pressures, will exhibit less expansion. In addition, accelerated setting and consumption of



• **Figure 8-13** Dimensional change of three amalgam products over a 24-hour period. **A**, A high-copper admixed amalgam with 50% mercury (Dispersalloy). **B**, A high-copper, single-composition amalgam with 42.5% mercury (Tytin). **C**, A lathe-cut, low-copper amalgam using a smaller size of alloy particles (Fine-Cut).

mercury also exhibit reduced expansion, including longer trituration times and the use of smaller alloy particles.

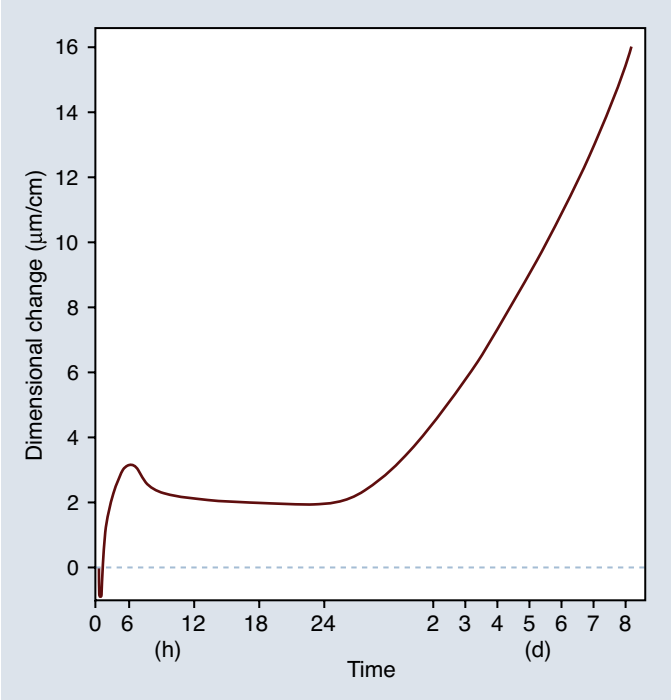
Measurements of the dimensional change of many modern amalgams reveal a net contraction (Figure 8-13), whereas in the past, measurements invariably indicated that an expansion occurred. The results conformed the model. Please note that older amalgams contained larger alloy particles and were mixed at higher mercury/alloy ratios than present-day amalgams. Likewise, hand trituration was used in preparing the specimens for earlier studies. Now, high-speed mechanical amalgamators are employed.

Effect of Moisture Contamination

When a zinc-containing, low-copper or high-copper amalgam is contaminated by moisture during trituration or condensation, a large expansion, such as that shown in Figure 8-14, can take place. This expansion usually starts 3 to 5 days after placement and may continue for months, reaching values as high as 4 µm/mm (0.4%). This type of expansion is known as **delayed expansion**. This expansion is caused by the hydrogen produced by electrolytic action involving zinc and water. The hydrogen gas collects within the restoration, increasing the internal pressure to levels high enough to cause the amalgam to creep, thus producing the observed expansion. Sources of contamination could include skin secretions by touching amalgam with bare hands or saliva from poor isolation of the operative field. Contaminants must be incorporated into the bulk of amalgam during trituration or condensation for delayed expansion to occur.

CRITICAL QUESTIONS

What is the phenomenon of marginal breakdown? What are the steps that can be taken to reduce the risk or extent of this process?



• **Figure 8-14** Delayed expansion of a low-copper conventional amalgam.

TABLE 8-2	Compressive Strength, Creep, and Tensile Strength of Low-Copper and High-Copper Amalgams			
	COMPRESSIVE STRENGTH (MPa)		Creep (%)	Tensile Strength at 24 Hours (MPa)
	1 Hour	7 Days		
Low copper*	145	343	2.0	60
Admix (high copper)†	137	431	0.4	48
Single composition (high copper)‡	262	510	0.13	64

* Fine Cut.

† Dispersalloy.

‡ Tytin.

Strength

A prime requisite for amalgam restorations is adequate strength to resist masticatory forces. In properly designed restorations, bulk fracture failures of amalgam restorations are relatively rare. More common are defects at the margins of amalgams. There is a difference of opinion on this subject as to whether the marginal defect is caused by fracture of the enamel or of the amalgam seen as **marginal breakdown**. This aspect will be discussed later.

Traditionally, the strength of dental amalgam has been measured under compressive stress using specimens of dimensions comparable to the volume of typical amalgam restorations. When strength is measured in this manner, the compressive strength of a satisfactory amalgam probably should be at least 310 MPa. Table 8-2 shows typical compressive and tensile strengths at 1 hour

and 7 days after preparation for a low-copper amalgam and two high-copper amalgams.

The strength of amalgam is more than adequate to withstand potential compressive loads. However, the amalgam is much weaker in tension than in compression (Table 8-2). Tensile stresses can readily occur in amalgam restorations. For example, a compressive pressure on a cusp of a restored tooth introduces complex stresses that result in tensile stresses in the isthmus of the restoration. It is important to reemphasize that amalgam cannot withstand high tensile or bending stresses. The design of the restoration should include supporting structures whenever there is a danger that the restoration will be flexed or pulled in tension. The use of a high-copper amalgam will not help because the tensile strengths of high-copper amalgams are not significantly different from those of the low-copper amalgams.

Effect of Trituration

The trituration time and the speed of the amalgamator dictate the effect of trituration. Either undertrituration or overtrituration will decrease the strength for both conventional and high-copper amalgams.

Effect of Mercury Content

Insufficient mercury between particles yields a dry, granular mix. Such a mix results in a rough, pitted surface that promotes corrosion. Increasing the final mercury content increases the volume fraction of the matrix phases. A higher mercury content promotes the formation of the γ_2 phase, even in a high-copper amalgam, and a greater incidence and severity of fracture will occur as the amalgam restorations age. The effect of the mercury content on the compressive strength of amalgam is shown in Figure 8-15.

Effect of Condensation

Good condensation techniques express mercury and result in a smaller volume fraction of matrix phases. Higher condensation pressures are required for the lathe-cut amalgams. In the case of the spherical amalgam, lighter pressures produce adequate strength, whereas greater condenser pressures just simply punch through the amalgam.

Effect of Porosity

Voids and porosity are factors that may reduce the compressive strength of set amalgams. The lack of plasticity of amalgam mixes caused by delayed condensation or undertrituration leads to porosity in set amalgams. Insufficient condensation pressure on lathe-cut alloys results in more porosity.

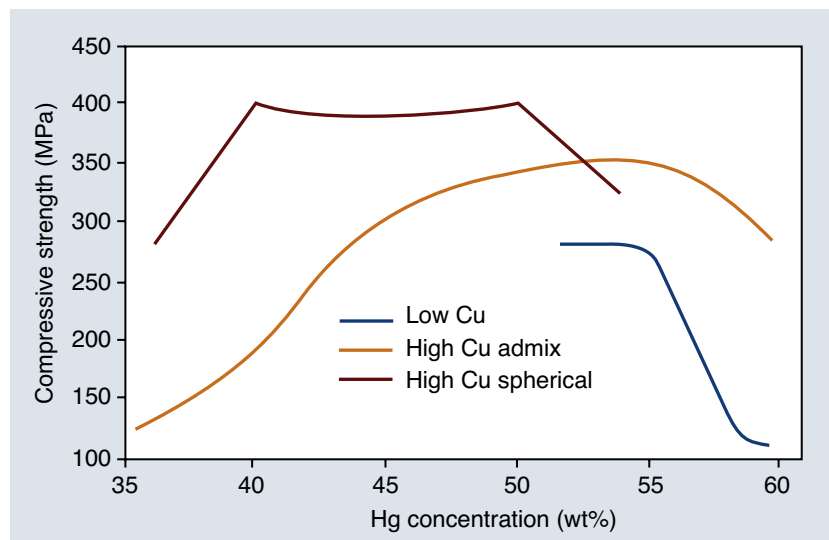
Effect of Amalgam Hardening Rate

Because a patient may be dismissed from the dental chair within 20 minutes after trituration of the amalgam, a vital question is whether the amalgam has gained sufficient strength to prevent fracture caused by a prematurely high occlusal force imposed by the patient. When the patient is dismissed, the compressive strength of the amalgam may be only 6% of the 1-week strength. Thus a high percentage of fractures in amalgam restorations likely occur within the first few hours after insertion.

ADA Specification No. 1 stipulates a minimum compressive strength of 80 MPa at 1 hour. The 1-hour compressive strength of high-copper, single-composition amalgams is exceptionally high (Table 8-2). This strength will make fracture less probable if the patient accidentally bites on the restoration soon after leaving the dental office. In addition, these amalgams may be strong enough shortly after placement to permit amalgam buildups to be prepared for crowns and allow earlier impressions of crown preparations to be made. Nonetheless, patients should be warned not to subject the restoration to high biting forces for at least 8 hours after placement. By that time, a typical amalgam will have reached at least 70% of its strength.

Creep

Creep occurs when a solid material slowly deforms plastically under the influence of constant stresses. Recall from the earlier discussion on delayed expansion that this is a form of creep caused by the constant pressure from the formation of hydrogen gas within moisture-contaminated zinc-containing amalgam. The other example of creep is when the protruded segment of amalgam at the margin of the restoration fractures and leaves a ditch



• **Figure 8-15** Effect of mercury content (percent by weight) on the compressive strength of amalgam prepared with representative low-copper; high-copper admix; and high-copper, single-composition spherical alloys.



• **Figure 8-16** Two surface amalgam restorations from (left) a low-copper amalgam with severe marginal breakdown and (right) minimal marginal discrepancy of a higher-quality amalgam restoration produced from a high-copper admix alloy. Both amalgams were placed at the same time. (Adapted from *Quality Evaluation of Dental Restorations: Criteria for Placement and Replacement*, Chicago, 1989, Quintessence.)

around the margin. **Figure 8-16** shows the difference in marginal breakdown produced with high- and low-creep amalgams. The creep of amalgam is determined by placing a cylinder of set amalgam (4 mm in diameter and 6 mm long) under a 36-MPa compressive stress. The specimen is prepared and stored at 37 °C for 7 days before testing. The change in length between 1 and 4 hours as a percentage of the original length is the creep value reported in **Table 8-2**.

When an amalgam creeps clinically, the γ_1 phase is the one that deforms plastically. Higher creep rates should be expected for amalgam with higher γ_1 volume fractions, and vice versa. The presence of the γ_2 phase increases the creep rate. In addition to the absence of the γ_2 phase, the very low creep rates in single-composition, high-copper amalgams may be associated with η' -phase rods, which act as barriers to deformation of the γ_1 phase. Therefore the manipulative factors discussed previously that maximize strength also minimize creep for any given type of amalgam.

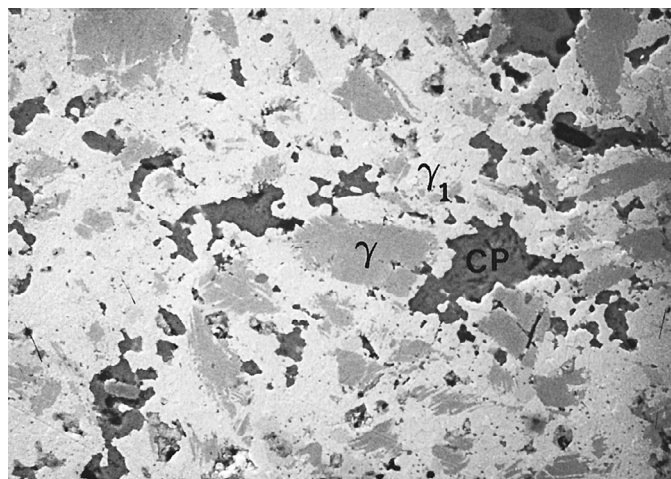
CRITICAL QUESTION

How can corrosion of an amalgam restoration lead to both positive and negative outcomes?

Tarnish and Corrosion Resistance

Amalgam restorations often tarnish and corrode in the oral environment. A tendency toward tarnish, which is the result of silver sulfide forming on the surface, does not affect or change the mechanical properties of the amalgam. Corrosion, on the other hand, has a negative effect on the properties. The most common corrosion products found with conventional amalgam alloys are oxides and chlorides of tin. These are found at the tooth–amalgam interface and within the bulk of amalgam restorations (**Figure 8-17**).

There is indirect evidence that the γ_2 phase is implicated in both marginal failure and active corrosion in conventional alloys but is not likely for the γ_2 -free high-copper alloys. The η' phase, which is less susceptible to corrosion than the γ_2 phase, exhibits limited corrosion with high-copper amalgams. Every effort should



• **Figure 8-17** Microstructure of 7-year-old conventional amalgam alloy filling. The various phases are marked. Note extensive porosity, and that the γ_2 area has been replaced by a Sn-Cl corrosion product (CP). (Courtesy Dr. Gary W. Marshall, Jr. and Dr. Sally J. Marshall.)

be made to produce a smooth, homogeneous surface on a restoration in order to minimize tarnish and corrosion, regardless of the alloy system used.

Whenever a gold restoration is placed in contact with an amalgam, corrosion of the amalgam can be expected as a result of the large differences in electromotive force (EMF) of the two materials (**Chapter 3, Dissimilar Metals**). The corrosion process can liberate free mercury, which can contaminate and weaken the gold restoration. Biological effects such as galvanism can also result.

Concern has been expressed that if high-copper amalgam restorations were placed in the same mouth with existing restorations of conventional amalgam, corrosion and failure could be accelerated with conventional amalgam. Clinical observations do not indicate accelerated corrosion in such situations. Laboratory models designed to monitor corrosion in adjacent restorations suggest that the current-flow paths are such that the electrochemical interaction between restorations is minimal.

Clinical Performance of Amalgam Restorations

Amalgam does not adhere to the tooth structure. At best, amalgam affords only a reasonably close adaptation to the walls of the prepared cavity. For this reason, cavity varnishes are used to reduce the gross leakage that occurs around a new restoration. Dentin bonding agents have been used in amalgam restorations to reduce microleakage. However, there is no evidence either to claim or refute a difference in survival between bonded and nonbonded amalgam restorations. Nonetheless, bonded amalgam may allow more conservative cavity preparations with reduced mechanical retentive features.

If the amalgam is properly inserted, leakage decreases as the restoration ages in the mouth. This is likely caused by corrosion products that form at the interface between the tooth and the restoration, sealing the interface, thereby preventing leakage. The ability to seal against microleakage is shared by both the older, low-copper amalgams and the newer, high-copper amalgams. Detecting margins that may be open by a few micrometers, either

with the eye or with a dental instrument such as an explorer, is virtually impossible.

The ultimate lifetime of an amalgam restoration is determined by several factors: (1) the material, (2) the dentist and the assistant, and (3) the patient's environment. Changing dentists reduces the lifetime of amalgam and composite restorations by up to 30%. The first two parameters are the dominant factors controlling the amalgam performance during the early life of the restoration. As time proceeds, differences in the dynamics of the oral environment among patients contribute significantly to the variability in the deterioration process, particularly marginal ditching. Changes in the amalgam structure during clinical use and the survival of amalgam restorations of various types are discussed next.

Clinical Significance of Dimensional Change

There are several causes of excessive expansion of amalgam. One is insufficient trituration and condensation; the other is delayed expansion brought about by the contamination of the Zn-containing amalgam with moisture during trituration or condensation. When an amalgam restoration expands and becomes wedged tightly against the cavity walls, pressure develops in the pulp chamber and causes pain. Such pain may be experienced 10 to 12 days after the amalgam is inserted. If the restoration is not removed, a contaminated amalgam continues to expand, and the result may be a protruding restoration.

CRITICAL QUESTION

A patient reports pain on chewing 1 day after an amalgam restoration has been placed. What are the most likely causes of this condition, and what are the best solutions?

A patient who complains of pain 1 day after an amalgam restoration is placed cannot be suffering the effects of delayed expansion caused by moisture contamination. One should examine the surface of the restoration for shiny abrasion marks indicating the possibility of hyperocclusion. The pain will disappear soon after the occlusion is properly adjusted. Another possibility is the development of cracks in the tooth because of excessive tooth reduction and weakened cusps. This situation may require replacement of the amalgam and hooding of the weakened cusp or cusps, as is done with a cast onlay restoration. There is also the possibility that the cracks are minor and do not threaten the integrity of the cusps or the vitality of the tooth. In this case, etching of the crack walls and bonding of the fissure may provide a sufficient interim solution. The last resort is to restore the tooth with an onlay or full crown to minimize the risk of tooth fracture.

CRITICAL QUESTIONS

Which variables affect the marginal breakdown of amalgam restorations? Which of these factors are under the control of the dentist?

Marginal Breakdown

Although the ditching of a margin (Figure 8-18) may not have progressed to the point where secondary caries may have developed, the restoration is unsightly, and further deterioration may be anticipated. Examination of clinical restorations has associated secondary caries with marginal discrepancies that exceed 50 μm . Many restorations are replaced as a preventive measure. Studies



• **Figure 8-18** A “ditched” amalgam restoration with severe marginal breakdown. (Courtesy Dr. Saulo Geraldelli.)

have shown that in a population with good oral hygiene, the incidence of secondary caries is quite low, even in the presence of severe marginal deterioration. Thus a more conservative approach, such as repair or refurbishing, has been suggested.

The creep rate has been found to correlate with the marginal breakdown of conventional low-copper amalgams; that is, the higher the amount of creep, the greater is the degree of marginal deterioration. There appears to be little correlation between creep and marginal breakdown with alloys having creep values below 1%. However, when creep values are above this level, restorations made from higher-creep alloys generally demonstrate greater marginal breakdown than do restorations of lower-creep alloys.

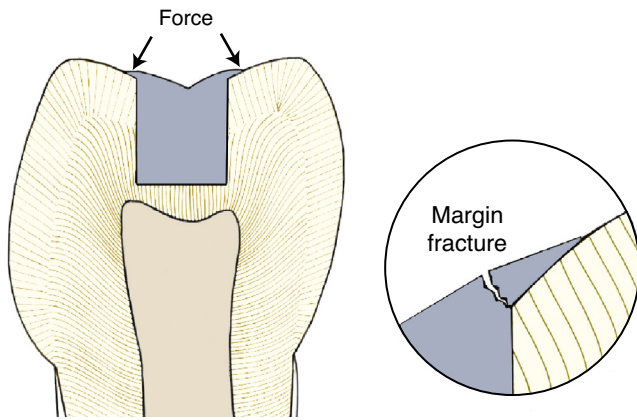
The absence of the corrosion-susceptible γ_2 phase in the microstructure of high-copper amalgams is assumed to be the principal factor responsible for the superior resistance of these alloys to marginal breakdown. If this assumption is correct, the property of creep is not an important property for the prediction of marginal breakdown in high-copper amalgams. Expansion of the amalgam from moisture contamination of a zinc-containing alloy can also cause this type of failure.

Thus several mechanisms, separately or working synergistically, may be responsible for marginal breakdown. At this time, the exact mechanism of marginal breakdown and these specific properties are not completely understood. However, selecting alloys that inherently have low creep and possess excellent resistance to corrosion is advisable.

Improper Cavity Preparation or Finishing

If unsupported enamel is left at the marginal areas of the cavity preparation, the tooth structure may fracture over time. Thus the ditched amalgam may involve fracture of the adjacent enamel as well as the amalgam.

Improper carving and finishing of the restoration and/or failure to remove a mercury-rich surface layer may leave a thin, weak ledge of amalgam extending over the enamel that will eventually fracture, leaving a ditched margin (Figure 8-19). Such thin extensions beyond the finish line of the tooth preparation are often difficult to detect and remove. One method is to finish the margins lightly with a soft, unribbed prophylactic polishing cup and a fine, slightly moist prophylaxis paste. However, the cup should be tilted such that the edge rotates from amalgam to tooth (Figure 8-11).



• **Figure 8-19** Marginal ditching of an amalgam restoration. If a feather edge of the amalgam is left overlapping the enamel at the margin or if a mercury-rich surface layer is not properly removed, the marginal extension may fracture under masticatory stress.

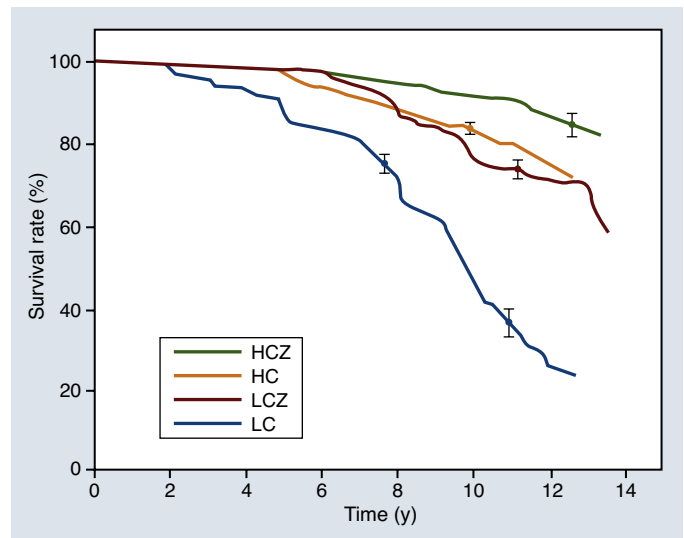
Survival of Amalgam Restorations

Although many factors may contribute to the deterioration of dental amalgams, as noted in the prior sections, the ultimate test is the long-term survival of the well-placed dental amalgam restoration. The longevity of amalgam restorations depends on whether they were placed in general practices or in controlled clinical studies. The median survival times for posterior amalgam restorations were 7 to 15 years in general practices. Larger, more complex restorations fall within the lower end of this range. Based on controlled clinical studies, dentists working under few time constraints for placement of restorations in motivated patients projected median survival times of 55 to 70 years.

Figure 8-20 is based on 14 independent controlled clinical studies in which the survival of amalgam restorations was rated in terms of their content of copper and zinc. Modern high-copper amalgams with Zn have the best overall survival of nearly 90% after 12 years. High-copper amalgams without Zn performed the next best, with survival rates of approximately 80%. The survival curves for these two groups of amalgams could be distinguished only after approximately 6 years, when the better survival of the high-copper systems containing a small quantity of Zn became apparent. The next group was composed of conventional low-copper amalgams with Zn. The worst performance was exhibited by low-copper amalgams that were Zn-free. These systems exhibited failures in 50% of the restorations after only 10 years. The reasons for the differences seen in this study are not completely clear. However, the combined and perhaps synergistic effects of the additional Cu and Zn contents probably offered increased corrosion protection to the restorations.

Repaired Amalgam Restorations

When part of an amalgam restoration fails, as from marginal fracture, this restoration can occasionally be repaired by condensing a new mix of amalgam directly on the remaining part of the existing restoration. The important factor related to the quality of the amalgam repair is the interfacial bond between the new and the existing amalgam. Surface treatment of the existing amalgam is a major factor in achieving a high-quality bond, as in tooth bonding (Chapter 6, *Cleanliness of the Bonding Surfaces*). The surface of an old amalgam to be bonded should be roughened to remove



• **Figure 8-20** Survival curves for amalgam restorations classified according to copper and zinc content. Both copper and zinc appear to provide protection to restorations. Thus in these clinical trials, many more high-copper restorations containing zinc survived than low-copper restorations without zinc. HC, high-copper amalgam without zinc; HCZ, high-copper amalgam with zinc; LC, low-copper amalgam without zinc; and LCZ, low-copper amalgam with zinc. (Adapted from Letzel H, et al: The influence of amalgam alloy on the survival of amalgam restorations: A secondary analysis of multiple controlled clinical trials. *J Dent Res* 76:1787–1798, 1997.)

corrosion and saliva contaminants and free of loose debris. When a freshly triturated amalgam is condensed directly onto the roughened surface of an existing amalgam, the flexural strength of the repaired structure can reach 50% of that of unrepaired amalgam. The repair should be attempted only if the area involved is one that will not be subjected to high stresses or one in which the two restoration parts are adequately supported and retained. Rubbing mercury on the repair site before condensing new amalgam or increasing the mercury content in the new amalgam can further improve the repair strength. Both approaches use mercury as a bonding agent but are discouraged because they increase the patient's exposure to mercury.

Making a slot on the existing amalgam to establish mechanical interlocking between the two materials also improves the quality of the repair joint if the slot can impede the crack growth. Some resin-based bonding agents appear to be superior when mechanical roughening of the surface could not be performed. The reaction between the unreacted amalgam alloy in the old amalgam and the mercury in the new amalgam is responsible for the bonding that occurs with repaired restorations. The use of a dentin bonding agent facilitates mostly mechanical retention to the amalgam surface but deprives the benefit of chemical bonding through mercury at the repaired interface.

Another repair option for areas that exhibit minor marginal breakdown—gaps that are 250 μm or less in width—is to etch the enamel adjacent to the restoration and, after rinsing and drying the marginal gap area, seal the gap with a dentin bonding adhesive. There is evidence from a 10-year study that bonded and sealed composite restorations placed directly over frank cavitated lesions extending into dentin arrested the clinical progress of these lesions for the duration of the study. Both sealed composite and conservative amalgam restorations exhibited superior clinical performance and longevity compared with unsealed amalgam restorations. This

repair option is promising but needs more clinical evidence to prove that this technique can prevent secondary caries.

The clinical diagnosis of secondary (recurrent) caries is the main reason for replacing amalgam restorations; fracture is the second most common reason for the failure of amalgam restorations. When secondary caries is diagnosed, replacement of the restoration often follows. An alternative treatment is to remove part of the restoration to the full depth at the site of the defect along with the infected tissue. Provided the main part of the restoration is satisfactory, the part of the restoration that was removed can then be filled with new amalgam or restored with resin-based composite. The repair of an existing restoration is now considered a viable and cost-effective alternative to complete replacement, as stated in numerous publications of clinical studies. However, there are no published randomized controlled trials that are reported according to the Consolidated Standards of Reporting Trials (CONSORT) statement per a Cochrane review of 2014. Clinicians should base their decisions on clinical experience and individual circumstances in conjunction with patients' preferences, where appropriate, when deciding whether to repair or replace the restoration.

CRITICAL QUESTION

A patient is concerned about the safety of amalgam restorations after hearing a news report on the toxicity of mercury. What quantifiable information can you provide to assure him that the levels of mercury vapor released from amalgam restorations are well below the known threshold levels for mercury toxicity?

Safety of Amalgam Restorations

The amalgam restoration is possible only because of the unique characteristics of mercury. Mercury is also the element that so markedly influences the basic properties necessary to clinical services. The safety issue of using mercury in the oral environment had been raised as early as when amalgams were introduced in North America in 1833. Some aspects of the current controversy and the future of the amalgam are discussed in this section. Additional information on the biocompatibility of mercury and amalgam is given in [Chapter 17, Dental Amalgam](#), on the biological effects of dental materials. To understand the possible side effects of dental amalgam, the differences between allergy and toxicity must be discussed.

Allergy

Typically, allergic responses represent an antigen–antibody reaction marked by itching, rashes, sneezing, and difficulty in breathing, with swelling or other symptoms. Contact dermatitis, which is a clinical sign of Coombs' type IV hypersensitivity reactions, represents the most likely pathological side effect of dental amalgam. When such a reaction has been documented by an allergist, an alternative material, such as a resin composite or ceramic material, must be used. However, none of these materials has yet been proven to be safer, in all respects, than dental amalgam.

Toxicity

Toxicity is the dose-related potential of a material to cause cell or tissue death. Some believe that mercury toxicity from dental restorations is the cause of certain undiagnosed illnesses, and that a real

hazard may exist for the dentist or dental assistant when mercury vapors are inhaled during mixing, placement, and removal. Most of the affected individuals documented in reports of mercury toxicity and allergic reactions attributable to dental amalgam were dentists or assistants (nurses) in a dental clinic. Few such cases have been reported during the past several decades, presumably because of improvements in encapsulation technology, capsule design, scrap storage methods, the elimination of carpets and other mercury-retention sites around dental offices, and the decreased use of amalgam. The matter has again come to the forefront with recent concerns about mercury pollution of the environment.

The patient's encounter with mercury vapor during insertion of the restoration is brief, and the total amount of mercury vapor released during occluding on amalgam restorations is far below the "no effect" level. Undoubtedly, small amounts of mercury are released during mastication. However, toxic reactions in the patient from these traces of mercury penetrating the tooth or sensitization from mercury salts dissolving from the surface of the amalgam are extremely rare.

Mercury Hygiene in Dental Offices

The potential hazards of mercury in dental offices can be greatly reduced by attention to a few precautionary measures. The operatory should be well ventilated. All excess mercury—including waste, disposable capsules, and amalgam removed during condensation—should be collected and stored in well-sealed containers. Debris of amalgam from cutting and grinding can be trapped by installing amalgam particle separators in the dental wastewater stream. The U.S. Environmental Protection Agency (EPA) required most dental offices nationwide to install amalgam particle separators by July 14, 2020. Proper disposal through reputable dental vendors is mandatory to prevent environment pollution. Amalgam scrap and materials contaminated with mercury or amalgam should not be incinerated or subjected to heat sterilization. If mercury is spilled, this must be cleaned up as soon as possible. Ordinary vacuum cleaners merely disperse the mercury further through the exhaust system. Mercury-suppressant powders are helpful but should be considered as temporary measures. If mercury encounters the skin, the skin should be washed with soap and water.

As noted earlier, the capsules, both reusable and single-use, that use a mechanical amalgamator should have a tightly fitting cap to avoid mercury leakage. When amalgam is being ground, a water spray and suction should be used. Eye protection, a disposable mask, and gloves are now standard requirements for dental practices.

The use of an ultrasonic amalgam condenser is not recommended. A spray of small mercury droplets has been observed surrounding the condenser tip during condensation. More detailed recommendations can be obtained by consulting the most recent reports of the ADA's Council on Scientific Affairs.

An important part of a program for handling toxic materials is periodic monitoring of actual exposure levels. Current recommendations suggest that this procedure be conducted annually. Several techniques are available. Instruments can be used that yield a time-weighted average for mercury exposure to air samples in the operatory. Film badges are also available that can be worn by office personnel in a manner like radiation exposure badges. Biological determinations can be performed on office staff to measure mercury levels in blood or urine. The risk from mercury exposure to dental personnel cannot be ignored, but close adherence to recommended hygiene procedures will help ensure a safe working environment.

Regulation of Amalgam Use by Governments

Currently, several countries are phasing out the use of dental amalgam because of environmental concerns. An important aspect of all these actions is the conclusion that, from a medical point of view, there is no clinical evidence to suggest that amalgam is causing illness in the general population.

Denmark published draft orders in 1989 proposing to discontinue the sale of all mercury-containing products, including dental amalgam, by 1999. In 1992, the Swedish parliament approved a general plan to phase out mercury from all sources, including amalgam in children's temporary teeth. The Swedish national health system stopped reimbursing patients for amalgam restorations in 1999. This decision greatly reduced the use of amalgam before a blanket ban on mercury took effect on June 1, 2009. In 2008, Norway announced a general ban on the use of mercury in products, which includes dental amalgam, with a 3-year phase-out period. Sweden and Denmark announced similar bans in the same year.

In 1996, Health Canada recommended that the use of amalgam should be avoided in the primary teeth of children, pregnant women, and patients with renal impairment. In addition, clinicians should use safe handling practices with mercury and provide information to patients on the benefits and risks of amalgam treatment. Austria, Germany, and Japan have similar restrictions on the use of dental amalgams. In Japan, the demand for mercury to be used in amalgam decreased from 5200 kg in 1970 to 100 kg in 2006. The annual emission of mercury into the air from amalgam in 2005 was estimated at about 3 kg. In 2009, the U.S. Food and Drug Administration (FDA) issued a final rule (FDA-2008-N-0163) classifying dental amalgam as a class II device. The FDA classification of all medical devices is discussed in detail in the risk classes of [Chapter 17, Legal Regulations and Risk Classes](#).

Selected Readings

- Anglen J, Gruninger SE, Chou NH, et al: Occupational mercury exposure in association with prevalence of multiple sclerosis and tremor among US dentists, *J Am Dent Assoc*, 146:659–668, 2015.
Occupational Hg exposure in U.S. dentists decreased over time and now is approaching that of the general population.
- Agnihotry A, Fedorowicz Z, Nasser M: Adhesively bonded versus non-bonded amalgam restorations for dental caries, *Cochrane Database Syst Rev*, (Issue 3), 2016.
This review only found one underreported trial. They concluded that there was no evidence to either claim or refute a difference in survival between bonded and non-bonded amalgam restorations.
- Bengtsson UG, Hylander LD: Increased mercury emissions from modern dental amalgams, *Biomaterials*, 30:277–283, 2017.
High-copper amalgams have been developed with focus on mechanical strength and corrosion resistance, but have been sub-optimized in other aspects, resulting in increased instability and higher emission of mercury vapor.
- Fédération Dentaire Internationale: Technical Report 33: Safety of dental amalgam, *Int Dent J*, 39:217, 1989.
This authoritative organization reviewed the literature on mercury toxicity and concluded that there is no documented scientific evidence to show adverse effects from mercury in amalgam restorations except in rare cases of mercury hypersensitivity.
- Letzel H, van't Hoff MA, Marshall GW, et al: The influence of amalgam alloy on the survival of amalgam restorations: A secondary analysis of multiple controlled clinical trials, *J Dent Res*, 76:1787–1798, 1997.

Although the policy of dental amalgam use is being revised in several countries, a global discussion on limiting the use of mercury products led by the United Nations Environmental Programme (UNEP) has adopted the conclusions from the Minamata Convention on Mercury that opened for signature at the Diplomatic Conference in Kumamoto, Japan, on October 10, 2013. There are 127 parties to the treaty as of January 2021. The treaty is a multilateral environmental agreement that addresses specific human activities that are contributing to widespread mercury pollution. The provision of the treaty related to dental amalgam is that the measures each party takes to phase down the use of dental amalgam shall allow for the party's domestic circumstances and relevant international guidance and shall include two or more of the measures listed in the document. They include setting national objectives of reducing caries and minimizing the use of amalgam, discouraging the use of amalgam through education and insurance policies, restricting use to encapsulated forms of amalgam if needed, promoting the use and research of cost-effective and clinically effective mercury-free alternatives, and promoting the use of best environmental practices in dental facilities to reduce releases of mercury and mercury compounds to water and land. Essentially, the convention calls for a phase-down approach to dental amalgam through greater emphasis on prevention, research into new dental materials, and best management practice. Current information on the Minamata Convention on Mercury can be found at <http://www.mercuryconvention.org>.

Acknowledgments

The author wishes to acknowledge Dr. G. W. Marshall, Jr., and Dr. S. J. Marshall for their previous contribution to the amalgam section of this chapter.

An analysis of multiple clinical trials demonstrated the synergistic effects of copper and zinc content on the survival of amalgam restorations.

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Mjör IA, Gordan VV: Failure, repair, refurbishing and longevity of restorations, *Oper Dent*, 27:528–534, 2002.

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Full Selected Readings for this chapter can be found on www.expertconsult.com.

Selected Readings (Web Version)

- Agnihotry A, Fedorowicz Z, Nasser M: Adhesively bonded versus non-bonded amalgam restorations for dental caries, *Cochrane Database Syst Rev*, (Issue 3), 2016.
This review only found one underreported trial. They concluded that there was no evidence to either claim or refute a difference in survival between bonded and non-bonded amalgam restorations.
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An analysis of multiple clinical trials demonstrated the synergistic effects of copper and zinc content on the survival of amalgam restorations.
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Galvanic interaction between cast gold and amalgam is reduced over time and surface treatments but is increased considerably when the amalgam contains zinc.

9

Metals

OUTLINE

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KEY TERMS

Age hardening Process of hardening certain alloys by controlled heating and cooling, which usually is associated with a phase change.

Annealing The process of controlled heating and cooling that is designed to produce desired properties in a metal. Typically, the annealing process is intended to soften metals, increase their ductility, stabilize shape, and increase machinability.

Antiflux A substance such as graphite that prevents the flow of molten solder on areas coated by the substance.

Base metal A metal that readily oxidizes or corrodes. Important base metals for dental alloys are nickel, cobalt, iron, titanium, and chromium.

Cold welding The metal-joining process by metallic bonding that does not rely on heating to achieve fusion but the pressure applied to the interface between parts to be joined; no liquid phase is produced within the interface joint.

CPTi Commercially pure titanium, which consists of 99 wt% or higher-purity titanium, with oxygen, carbon, nitrogen, and hydrogen dissolved interstitially.

Dislocation An imperfection in the crystalline arrangement of atoms consisting of an extra partial plane of atoms (edge dislocation), a spiral distortion of normally parallel atom planes (screw dislocation), or a combination of the two types.

Flux Compound applied to metal surfaces that dissolves or prevents the formation of oxides and other undesirable substances that may reduce the quality or strength of a soldered or brazed area.

Grain growth The increase in the mean crystal size of a polycrystalline metal produced by a heat-treatment process.

Grain refinement The process of reducing the crystal (grain) size in a solid metal through the action of specific alloying elements or compounds; the process increases the yield strength of metals.

Lost wax technique Process in which a wax pattern, prepared in the shape of missing tooth structure, is embedded in a casting investment and burned out to produce a mold cavity into which molten metal is cast.

Noble metal Gold and platinum group metals (platinum, palladium, rhodium, ruthenium, iridium, and osmium), which

are highly resistant to oxidation and dissolution in inorganic acids.

Precipitation hardening The process of strengthening and hardening a metal by precipitating a phase or constituent from a saturated solid solution.

Recovery A stage of heat treatment that results in the partial restoration of properties of a work-hardened metal without a change in the grain structure.

Recrystallization The process of forming new stress-free crystals in a work-hardened metal through a controlled heat-treatment process.

Soldering Process of building up a localized area of a metal prosthesis with a molten filler metal or joining two or more metal components by heating them to a temperature below their solidus temperature and filling the gap between them using a molten metal with a lower liquidus temperature. If the melting temperature of the solder is greater than 450 °C, the process is called *brazing*.

Springback The amount of elastic strain that a metal can recover when loaded to and unloaded from its yield strength; an important property of orthodontic wires.

Strain hardening The increase in strength and hardness and decrease in ductility of a metal that is caused by permanent deformation below its recrystallization temperature; also called *work hardening* or *cold working*.

Superelasticity The ability of certain nickel-titanium alloys to undergo extensive elastic deformation resulting from a stress-assisted phase transformation, with the reverse transformation occurring on unloading; sometimes called *pseudoelasticity*.

Welding Process of fusing two or more metal parts through the application of heat, pressure, or both, with and without a filler metal, to produce a localized union across an interface between the workpieces.

Working range The maximum amount of elastic strain that an orthodontic wire can sustain before it permanently deforms.

Wrought alloy A metal that has been permanently deformed to alter the shape of the structure and certain mechanical properties, such as strength, hardness, and ductility.

In his 1907 U.S. Patent 865823, Taggart described a method of making gold inlays using the lost **wax technique**. The lost wax method of making metal objects involves pouring a molten metal into a mold that has been created with a wax pattern ([Chapter 14, Wax Pattern and Sprue Design](#)). The process led to making custom precision casts for the restoration of missing tooth structure, such as onlays, crowns, multiple-unit fixed dental prostheses (FDPs), and frameworks for removable partial dentures (RPDs). Since the early 1980s, the numbers of dental alloys, along with new alloy systems, have increased dramatically as a result of the market-price increase of **noble metals**, the performance of the same function at a lower cost, the need for increasingly specialized physical and mechanical properties, and the awareness of the importance of biological properties.

Objects of any design, intricate or simple, can be produced by using the lost wax technique as long as a wax pattern can be made and invested, and alloys can be melted, or by using alternative processing techniques such as computer-aided design/computer-aided manufacturing (CAD-CAM) milling and three-dimensional (3-D) printing. On the other hand, many ancillary dental materials and instruments are fabricated from initially cast alloys that have been subsequently rolled to form sheets or rods, drawn into wire or tubing, or forged into a finished shape. Rolling, drawing, and forging are major processes of permanently deforming metals.

Whenever a cast pure metal or alloy is permanently deformed to an intended shape in any manner, it is considered a **wrought alloy**. This permanent deformation alters the microstructure, and the alloy exhibits properties that are different from those it had in the as-cast state. The most significant change is the increase of yield strength with a reduction in ductility. The applications of wrought alloys in dentistry include orthodontic wires, clasps for RPDs, root canal files and reamers, preformed crowns in pediatric dentistry, and surgical instruments. Most metal-based restorations and prostheses are cast and not wrought.

In the construction of dental appliances, there is often a need to join metal parts, cast or wrought, together using high heat. When wrought alloys are involved in such joining, the strength and fracture resistance of the wrought alloy will be compromised if the metal is exposed to the temperature range at which the wrought structure is diminished or lost. Such weakening can occur during the metal-joining process for stainless-steel orthodontic appliances.

The ability to work with dental alloys and associated wrought alloys is dependent on a knowledge of these materials. The goal of this chapter is for the reader to become familiar with various types of casting alloys and associated wrought alloys. We will discuss the desirable properties and the relevant mechanical properties of dental alloys first. For casting alloys, the focus is the alloy classification and clinical applications of the alloys. For wrought alloys, the focus is the process of permanent deformation and its effect on the properties for their specific applications in dentistry. Several types of wrought alloys used in dentistry are described. The description of joining metals is like that for bonding presented in [Chapter 6](#); the emphasis is on the principles and procedures of the process.

As previously done in [Chapter 2, Metals](#), the terms *metal* and *alloy* are frequently used interchangeably.

Desirable Properties of Dental Alloys

Depending on the primary purpose of the prosthesis, the choice of casting alloy is made by the dentist in collaboration with a qualified dental laboratory technician or technologist. From the

standpoint of patient safety and the risk of medico-legal issues, it is highly important to understand the following clinically important requirements and properties of dental casting alloys:

1. **Biocompatibility**—The alloy must tolerate oral fluids and not release any harmful products into the oral environment that might cause a toxic or allergic reaction. Biocompatibility will be covered in [Chapter 17](#).
2. **Tarnish and Corrosion Resistance**—*Corrosion* is the physical deterioration of a material in the oral environment, and *tarnish* is a thin film that is adherent to the metal surface ([Chapter 3, Tarnish and Corrosion](#)). Both phenomena affect the durability and appearance of the prostheses.
3. **Thermal Properties**—The melting range of the casting alloys must be low enough to form smooth surfaces with the mold wall of the casting investment ([Chapter 14, Investment Materials](#)). For metal-ceramic prostheses, the alloys must have closely matching thermal expansion coefficients to be compatible with the given porcelains, and they must tolerate high processing temperatures without deforming via a creep process.
4. **Strength Requirements**—The alloy must have sufficient strength for the intended application. For example, alloys for bridgework require higher strength than alloys for single crowns.
5. **Fabrication**—The molten alloy should flow freely into the investment mold, without any appreciable interaction with the investment material, and wet the mold to form a surface free of porosity. It should be possible to cut, grind, finish, and polish the alloy to obtain a prosthesis with a satisfactory surface finish.
6. **Porcelain Bonding**—The alloy must be able to form a thin adherent oxide that enables chemical bonding to ceramic veneering materials.
7. **Economic Considerations**—The cost of metals used for single-unit prostheses or as frameworks for FDPs or RPDs is a function of the metal density, fluctuations in metal prices, and the cost per unit mass.

Functional Mechanical Properties of Alloys

Mechanical properties are the measured responses of materials in the form of stress and strain under an applied force or distribution of forces. The relevant functional characteristics of casting and wrought alloys are described next.

CRITICAL QUESTIONS

What are two clinical disadvantages of cast metals that have lower elastic moduli? Why does a long-span bridge require alloys of high elastic modulus?

Elastic Modulus

One characteristic of a material with a high elastic modulus is its rigidity or stiffness. For a dental prosthesis, rigidity is equivalent to the resistance to flexure (bending). When a long-span FDP flexes during occluding of the pontic, the mesiodistal bending moment exerted on the abutment teeth can act as a dislodging force, lifting the mesial and distal aspects of the prosthesis. Furthermore, a flexing bridge can induce lateral forces on the abutment teeth, resulting in the loosening of these teeth. For a metal-ceramic prosthesis, the overlying brittle porcelain will fail catastrophically when the metal substructure flexes beyond the flexural limit of the ceramic. The elastic modulus is also important for the major connectors of an RPD, which must have enough rigidity to prevent flexure during the placement and function of the prosthesis.

Resistance to flexure also allows the clasps of an RPD to fit into areas of minimal undercuts and still provide adequate retention.

CRITICAL QUESTION

Why is it that a cast prosthesis that is subjected to tensile stress above the alloy yield strength will not necessarily fracture?

Yield Strength (Proof Stress)

Recall the discussion in [Chapter 4, Stress-Strain Properties](#) that yield strength, elastic limit, and proportional limit, by definition, are different properties, but all three terms have been used to reflect the capacity of a cast prosthesis to withstand mechanical stresses without permanent deformation. Ideally, dental alloys should have a high yield strength so that a large amount of stress must be applied before a permanent change in dimensions occurs. For an orthodontic appliance, it relates to the maximum force the wire can deliver. Generally, alloys with tensile yield strengths above 300 MPa function satisfactorily in the mouth.

CRITICAL QUESTION

How does the alloy ductility increase the fracture resistance of a margin of a cast metal crown or a clasp arm on an RPD?

Ductility (Percent Elongation)

Ductility represents the amount of permanent deformation under tensile stress that an alloy can undergo before it fractures. If the force applied is in a compressive mode, the property is called *malleability*. A reasonable amount of ductility and malleability is essential if a prosthesis requires adjustment to be functional, such as the bending of RPD clasps and the burnishing of crown margins. As discussed earlier, one needs to apply stress greater than the yield strength of the material to cause permanent deformation on a metal surface. Therefore, high ductility allows one to achieve more permanent deformation without fracture but does not indicate if burnishing or adjusting the prosthesis would be easier or more difficult in terms of the stress required.

CRITICAL QUESTION

Why is a harder metal more resistant to wear than a softer metal?

Hardness

Clinically, hardness reflects the resistance of the restoration to scratching and abrasion by the opposing tooth or restoration and the ability to maintain the smoothness of the prosthesis in the oral environment. However, a harder restoration surface can cause excessive wear of softer opposing dentition or restorations. In addition, harder surfaces are more difficult to cut, grind, finish, and polish because higher stress is required for each procedure.

Fatigue Resistance

Fatigue failure can occur when a material is subjected to repeated loading and unloading below its elastic limit. Most fractures of prostheses and restorations develop progressively over many stress cycles of loading and unloading. When the load is above a certain threshold, crack propagation is initiated from flaws within

the prosthesis. Eventually, a crack propagates to a critical size, and sudden fracture occurs. Common engineering expressions of fatigue fracture resistance are fatigue strength and endurance limit ([Figure 4.15](#)). *Fatigue strength* (S_N) is defined as the stress at which failure occurs after a specific number of fatigue cycles. *Endurance limit* is the maximum stress that can be maintained without failure over an infinite number of cycles. Some alloys do not have a well-defined endurance limit.

Classification of Dental Casting Alloys

In 1932, the dental materials group at the National Bureau of Standards (now National Institute of Standards and Technology) classified dental gold alloys being used then by Vickers hardness number (VHN): type I (soft, VHN 50 to 90), type II (medium, VHN 90 to 120), type III (hard, VHN 120 to 150), and type IV (extra hard, VHN 150 and above). Since then, the number of alloy compositions and applications has increased vastly. They are now classified according to composition, intended usage, or mechanical properties.

Alloy Classification by Noble Metal Content

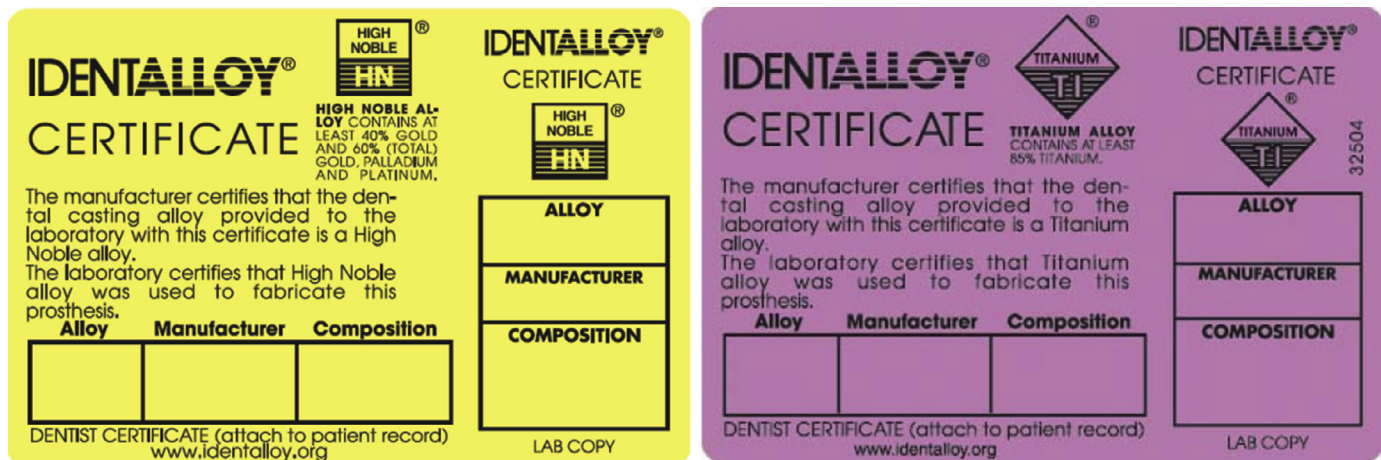
In 1984, the American Dental Association (ADA) proposed a simple classification for dental casting alloys based on the content of noble metals. Three categories were described: high noble (HN), noble (N), and predominantly **base metal** (PB). Subsequently, a fourth group of titanium and titanium alloys was added because of the unique characteristics of titanium. This classification is presented in [Table 9-1](#). Noble metals comprise a group of seven metals that are resistant to corrosion and tarnish in the mouth. In order of increasing melting temperature, they include gold, palladium, platinum, rhodium, ruthenium, iridium, and osmium. These noble metals and silver are sometimes called *precious metals*, referring to their high economic value, but the term *precious* is not synonymous with *noble*. Silver is reactive in the oral cavity and is not a noble metal.

Based on this classification, the IdentAlloy program was established by manufacturers to provide documentation of certified alloys. Under this program, each alloy has a certificate ([Figure 9-1](#)) that lists its manufacturer, alloy name, composition, and ADA classification. Some insurance companies use it as well to determine the cost of crown and bridge treatment. Keep in mind that this system certifies only the composition of alloys.

TABLE 9-1 Alloy Classification by Noble-Metal Content—American Dental Association (2003)

Alloy Type	Total Noble-Metal Content
High noble (HN)	Must contain $\geq 40\%$ Au and $\geq 60\%$ by weight of noble-metal elements*
Noble (N)	Must contain $\geq 25\%$ by weight of noble-metal elements
Predominantly base metal (PB)	Contains $< 25\%$ by weight of noble-metal elements
Titanium and titanium alloys	Titanium $\geq 85\%$ by weight

*Noble-metal elements include Au, Pd, Pt, Rh, Ru, Ir, and Os.



• **Figure 9-1** Examples of IdentAlloy certificate.

Alloy Classification by Mechanical Properties

The historic ADA Specification No. 5, which originally had composition ranges for the component elements in the four types of gold casting alloys, evolved to stipulating mechanical property requirements for yield strength, percentage elongation, and Vickers hardness. The relevant current standard is International Organization for Standardization (ISO) 22674:2016, which classifies metallic materials for fixed and removable restorations and appliances into six types according to yield strength and elongation, regardless of noble metal contents (Table 9-2).

Alloy Classification by Principal Elements

Alloys may be classified based on the principal or most abundant element (e.g., a palladium-based alloy), or they may be named based on the two or three most important elements (e.g., Pd-Ag, Co-Cr, or Ni-Cr-Be alloys). The components are listed in decreasing order of weight percent. An exception to this rule is the identification of elements that substantially affect the properties of the alloy. For example, Ni-Cr-Mo-Be alloys are often designated as *Ni-Cr-Be alloys* because of the contributions of beryllium to the control of castability and surface oxidation at high temperatures and the relative health-hazard potential of beryllium compared with other metals. *Castability* refers to the ease of making quality castings. Excellent websites to view the wide range of dental alloy compositions include Argen at <https://argen.com/>.

Alloy Classification by Dental Applications

There are three categories of dental casting alloys designated by application: all-metal fixed prostheses, metal-ceramic prostheses, and RPDs. Each type of alloy classified by noble metal content (Table 9-1) is available in all three categories. One may use high-noble and noble alloys intended for metal-ceramic prostheses to fabricate all-metal prostheses. However, alloys for all-metal restorations, which can deform or melt during porcelain-firing, should not be used to make metal-ceramic restorations.

Base-metal and titanium alloys, on the other hand, are often marketed for both all-metal and metal-ceramic prostheses because of their oxide formation at room temperature. In this chapter, dental alloys are discussed by their applications.

TABLE 9-2 Classification of Metallic Materials for Dental Applications—ISO 22674 (2016)

Type	Yield Strength (MPa)	Elongation (%)	Examples of Applications
0 ¹	—	—	Single-tooth fixed restorations—for example, small veneered one-surface inlays, veneered crowns
1	80	18	Single-tooth fixed restorations, veneered or nonveneered one-surface inlays, veneered crowns
2	180	10	Single-tooth fixed restorations—for example, crowns or inlays without restriction on the number of surfaces
3	270	5	Multiple-unit fixed restorations—for example, bridges
4	360	2	Appliances with thin cross sections that are subjected to very high forces—for example, RPDs, clasps, thin veneered crowns, wide-span bridges or bridges with small cross sections, bars, attachments, implant-retained superstructures
5	500	2	Thin RPDs, parts with thin cross sections, clasps

ISO, International Organization for Standardization; RPD, removable partial denture.

¹Metallic materials for metal-ceramic crowns produced by electroforming or sintering belong to type 0.

Alloys for All-Metal Prostheses

These alloys are discussed in three main categories: noble (includes high-noble), predominantly base-metal, and titanium and titanium alloys.

High-Noble and Noble Alloys

The compositions of selected high-noble and noble alloys are given in Table 9-3. Their physical and mechanical properties are shown in Table 9-4. Gold and palladium are the two major elements that make up the nobility of noble and high-noble alloys; these alloys are discussed in two categories: Au-based alloys and Pd-based alloys.

Gold-Based Alloys

Referring to Table 9-2, type 1 alloys are designed for inlays that are not subjected to substantial mastication forces. Type 2 alloys having greater mechanical properties than type 1 are used for one-surface inlays. Type 3 alloys are used for constructing crowns, bridge abutments, and inlays, which are subjected to great stress during mastication. Type 4 alloys are used in high-stress areas such as bridges and RPD frameworks (although the

gold-based RPD is now rare). The alloys for bridge and RPD framework constructions must be sufficiently rigid to resist flexure, possess high yield strength to prevent permanent distortion, and be ductile enough for adjustment if the clasp of a framework has been distorted or needs adjustment.

Various elements have been incorporated into gold alloys to produce alloys with suitable properties. For example, platinum and palladium increase the hardness and elastic modulus of gold and raise the melting temperature of the alloy. A higher melting temperature is beneficial when components are to be joined by soldering. Copper in a sufficient quantity relative to the gold content renders the alloy heat-treatable (Chapter 2, Gold-Copper System) but can alter the color of the alloy. Silver forms solid solutions with gold and palladium and is effective in neutralizing the reddish color of copper in gold-copper alloys. Palladium has a good range of solubility with gold, silver, and copper, resulting in good mechanical properties and improvement of tarnish and corrosion

TABLE 9-3 Typical Compositions of High-Noble and Noble Alloys for All-Metal Prostheses								
Alloy Type	Color	ELEMENTAL COMPOSITION (PERCENT BY WEIGHT)						
		Au	Pd	Ag	Cu	Pt	In	Balance*
1	Yellow	83	0.5	10	6	—	—	Zn; Ir
2	Yellow	82	—	—	—	18	—	Ir
	Yellow	77	1	13	8.5	—	—	Zn; Ir
3	Yellow	74.5	3.5	11	10.5	—	—	Zn; Ir
	Yellow	50	4	35	10	—	—	Zn; Ir
	Yellow	2	34.9	30	—	—	30	Zn:3; Ir
	White	—	25	71.5	—	—	2.5	Zn; Ru
4	Yellow	60	4	20.5	15	—	—	Zn; Ir
	Yellow	50	3	26	11.5	—	3	Zn:1; Ir
	Pale yellow	20	20	36	—	—	18	Zn:6; Ir
	White	4	30.3	45.7	18.5	—	—	Zn:1.5; Ir

*Elements without a value are less than 1% by weight.

TABLE 9-4 Physical and Mechanical Properties of Some Modern High-Noble and Noble Alloys for All-Metal Prostheses						
Alloy Type	ADA Classification	Density (g/cm³)	Yield Strength (MPa; soft/hard)	Hardness (VHN; soft/hard)	Elastic Modulus (GPa)	Elongation (%; soft/hard)
1	High noble	16.6	126	85	70	51
2	High noble	19.2	146	95	50	23
	High noble	15.4	221	120	109	54
3	High noble	15.5	207/276	121/182	76	39/19
	Noble	13.2	309/648	138/225	104	28/15
	Noble	10.5	297	180	51	5–6
	Noble	10.5	248/310	145/155	55	10/8
4	High noble	14.5	350/607	165/235	88	35/4
	Noble	13.2	428/683	180/255	86	28/16
	Noble	11.3	420/530	165/220	103	10/2
	Noble	10.6	460/700	195/265	116	10/3

ADA, American Dental Association; VHN, Vickers hardness number.

resistance. Zinc acts as an oxygen scavenger during the melting and casting of noble and high-noble alloys.

CRITICAL QUESTIONS

What effects can the cooling rate of a heat-treated type 3 gold-copper alloy have on its hardness and ductility?

What happens within gold-copper alloys that are subjected to a prescribed heating-cooling cycle?

The underlying principles for heat treatment of these alloys have been discussed in [Chapter 2, Gold-Copper System](#). Briefly, the casting is placed in a furnace at 700 °C for 10 minutes, and then quenched in water to retain a disordered solid-solution phase with reduced yield strength and hardness but increased ductility. The process is called a solution heat treatment. The same casting is placed in a furnace with the temperature set between 200 and 450 °C for 15 to 30 minutes before quenching in water. The treatment produces regions of ordered solid-solution phase with increased yield strength and hardness but a reduction of elongation ([Table 9-4](#)). The process is called **age hardening**.

The softening heat treatment is indicated for prostheses that are ground or reshaped (permanent deformation) to a different form, either in or out of the mouth, to restore their ductility. Because the proportional limit is increased during age hardening, a considerable increase in the modulus of resilience can be expected. The hardening heat treatment is indicated for metallic RPDs, saddles, FDPs, and other similar structures where rigidity of the prosthesis is needed. For small structures, such as inlays, a hardening treatment is not usually required.

CRITICAL QUESTION

What characteristics of palladium make it a natural choice of element to replace gold for dental alloys?

Silver-Palladium Alloys

Silver-palladium alloys are often white and predominantly silver in composition and must contain at least 25% palladium to provide tarnish and corrosion resistance of the alloy. They may also contain copper and a small amount of gold to increase the ductility and improve the castability of the alloy for dental applications. Ag-Pd alloys can produce acceptable castings when close attention is paid to precise control of the casting and mold temperatures. Casting temperatures are in the range of those for yellow gold alloys. The copper-free Ag-Pd alloys may have physical properties similar to those of a type 3 gold alloy. With 15% or more copper, the alloy may have properties more like those of a type 4 gold alloy.

Indium and palladium at a 1:1 atomic ratio form a gold-color intermetallic compound. When the content of indium in a Pd-Ag alloy is 18% to 30% by weight, the alloy achieves a gold-like color. The colored phase of the Pd-In binary alloy system is hard and brittle and is not a strengthener. Iridium or ruthenium is added in small quantities to high-noble and noble alloy compositions for **grain refinement** because smaller grains improve the yield strength ([Chapter 2, Grain Refinement and Grain Size](#)).

CRITICAL QUESTION

What is the role of chromium in predominantly base-metal alloys? How does beryllium improve the properties of nickel-based alloys?

Predominantly Base-Metal Alloys

Currently, there are two main groups of base-metal dental alloys: nickel-chromium (Ni-Cr) and cobalt-chromium (Co-Cr). The Ni-Cr alloys can be further divided into those with and without beryllium, which improves castability and promotes the formation of a stable metal oxide for porcelain bonding. The majority of Ni-Cr alloys are used for small castings such as crowns and FDPs, and Co-Cr alloys are primarily used for casting RPDs for which a high elastic modulus and yield strength are needed. [Table 9-5](#) lists the compositions and properties of selected base-metal alloys for all-metal and metal-ceramic applications.

Chromium, a critical element of base-metal alloys, oxidizes rapidly on the surface of the alloy to form a thin layer of chromium oxide, which prevents the diffusion of oxygen into the underlying metal and the corrosion process. Chromium in the bulk alloy also provides strengthening by solid-solution hardening. Molybdenum increases corrosion resistance and strength and decreases the thermal expansion coefficient of base-metal alloys. Higher thermal expansion is beneficial for porcelain bonding and minimizes the risk of porcelain cracking or fracture. Some minor elements are incorporated to improve manipulation and mechanical properties. For example, beryllium lowers the fusion temperature of the alloys, which improves castability, and refines grain size, which increases strength. Manganese and silicon also improve the castability of the alloys. Carbon forms carbides with other elements in the alloy, increasing the hardness and yield strength with a reduction in ductility. The aluminum in Ni-Cr alloys forms a nickel-aluminum compound, Ni_3Al , which increases both the yield strength and the tensile strength. Nitrogen, which is incorporated in the alloy during casting in ambient air, also improves the overall qualities of the casting.

The manipulation and mechanical properties of base-metal alloys are described in more detail in the following section on alloys for metal-ceramic prostheses and in the subsequent section on RPDs because base metals are used to a lesser extent for all-metal prostheses.

Titanium and Titanium Alloys

Titanium has a high melting point (1668 °C) and a high rate of oxidation above 900 °C. It requires a special casting machine with high-temperature melting capability in a nonoxidizing chamber. For example, an argon arc with a nonconsumable tungsten electrode or high-frequency induction is used for melting titanium alloys in crucibles made of copper, magnesia, or carbon and in an argon or helium atmosphere. A casting investment consisting of oxides, such as MgO , ZrO_2 , or Y_2O_3 , which are more stable than titanium oxide, is used to ensure acceptable castability. Centrifugal force, casting-pressure difference, and gas pressure have been used to force the molten-metal flow into the mold. Titanium can react with the investment material during casting and forms a very hard surface layer called α -case, with a thickness up to 150 μm . The VHN of cast commercially pure titanium increases from a bulk value of nearly 200 to approximately 650 at a depth of 25 μm below the surface. Special instruments are required in the dental laboratory for finishing and adjusting titanium castings.

Titanium derives its corrosion protection from a thin passivating oxide film (about 10 nm thick), which forms spontaneously with the surrounding oxygen. Titanium is considered the most biocompatible metal used for dental restorations and prostheses.

TABLE 9-5 Typical Compositions and Mechanical Properties of Base-Metal Alloys for Crown, FDP, and Metal-Ceramic Applications

Alloy (Supplier)	COMPOSITION (PERCENT WT)					MECHANICAL PROPERTIES			
	Ni	Co	Cr	Mo	Balance*	Yield Strength (MPa)	Hardness (VHN)	Elastic Modulus (GPa)	Elongation (%)
IPS d.Sign 15 (Ivoclar)	58.7	1	25	12.1	Fe:1.9; Si:1.7; Ce	340	230	200	13
Rexalloy (Pentron Alloys/Argen)	67	—	14	8	Ga:8; Al; Fe; Si; Mn; Zr; Cu	300	177	191	27
Heraenium S (Heraeus Kulzer)	62.9	—	23	10	Si:2; Fe:15.5; Ce:0.5	310	220	224	29
NPX-III (CMP Industries)	76.5	x†	14	4.5	Al:2.5; Be:1.6; Ti	784	350	200	9
Argeloy Bond (Argen)	77	—	14	4.7	Mn; Fe; Si; C	630	370	207	10
Norex (Pentron Alloys/Argen)	—	55	25	—	W:10; Ru:5; Al; Nb, Y, Zr	621	350	204	7
Heraenium P (Heraeus Kulzer)	—	59	25	4	W:10; Si:1; Mn:0.8; N	650	330	200	8
Jelbond Supreme (Jelenko Alloys/Argen)	—	61	27	6	W:5; Mn; Si; Fe; C	475	365	223	8

FDP, fixed dental prosthesis; VHN, Vickers hardness number.

*Elements without a value are less than 1% by weight.

†x indicates trace amount.

TABLE 9-6 Tensile Properties and Impurity Limits for Unalloyed (CP) Titanium (ASTM F67)*

Designation	PHYSICAL PROPERTIES (MINIMUM)				IMPURITY LIMITS (max), PERCENT BY WEIGHT				
	Tensile Strength (MPa)	Yield Strength (MPa)	Hardness (VHN)	Elongation (%)	N	C	H	Fe	O
Grade 1	240	170	126	24	0.03	0.08	0.015	0.20	0.18
Grade 2	340	280	178	20	0.03	0.08	0.015	0.30	0.25
Grade 3	450	380	221	18	0.05	0.08	0.015	0.30	0.35
Grade 4	550	480	263	15	0.05	0.08	0.015	0.50	0.40

ASTM, American Society for Testing Materials; VHN, Vickers hardness number.

*Elastic modulus is approximately 110 GPa for each type.

Commercially Pure Titanium

According to the American Society for Testing and Materials (ASTM) Standard F67, there are four unalloyed grades of commercially pure titanium (**CP Ti**) based on the concentration of impurities (**Table 9-6**). The elastic modulus of CP Ti is comparable to that of tooth enamel and noble alloys, but it is lower than that of other base-metal alloys (**Table 9-5**). CP Ti is often selected for its excellent corrosion resistance, especially in applications for which high strength is not required. The major strengthening element is oxygen. Increasing the oxygen content of CP Ti increases not only the flexural strength but also the fatigue strength.

CRITICAL QUESTIONS

Why is a Ti-Al-V alloy with high strength not always preferred to the commercially pure titanium metal for dental prostheses? How do alloying elements affect the properties of titanium dental alloys?

Titanium Alloys

CP Ti undergoes an allotropic (polymorphic) transformation from a hexagonal close-packed crystal structure (α phase) at 882 °C to a more ductile body-centered crystal structure (β phase). By incorporating a combination of α - and β -phase stabilizers, four possible types of titanium alloys can be produced: α , near- α , α - β , and

TABLE 9-7 Properties of Two α - β Titanium Alloys for Dental Prostheses

Alloy	Elastic Modulus (GPa)	Yield Strength (MPa)	Hardness (VHN)	Elongation (%)
Ti-6Al-4V	117	860	320	10–15
Ti-6Al-7Nb	105	795	330	10

VHN, Vickers hardness number.

β . Alpha-phase stabilizers, such as aluminum, carbon, nitrogen, and gallium, raise the temperature for transforming α to β phase on heating. Beta-phase stabilizers, such as molybdenum, cobalt, nickel, niobium, copper, palladium, tantalum, and vanadium, lower the temperature for transforming β to α phase on cooling. Alpha alloys will form no β phase on cooling. Near-alpha alloys will form a limited amount of β phase on cooling. Alpha-beta alloys are metastable, which makes them heat-treatable and will contain both phases at room temperature. Thermal treatment dictates the relative amount of α and β phases and mechanical properties. Beta alloys contain sufficient beta stabilizers to retain the β phase on cooling; they can be solution-treated and aged to improve strength.

The most widely used titanium alloy in dentistry and for general engineering applications is Ti-6Al-4V, which is an α - β alloy. Although this alloy has greater strength than CP Ti, it is not as attractive for dentistry and biomedical applications because of some concerns about health hazards from the slow release of aluminum and vanadium. Vanadium in high doses is highly toxic, and aluminum has been reported to cause potential neurological disorders. Niobium has not been associated with any known toxic or adverse reactions in the body and belongs to the same group as vanadium in the periodic table. Replacing vanadium in Ti-6Al-4V with the same atomic percentage of niobium yields Ti-6Al-7Nb. Both alloys are considered to be acceptable for biomedical applications. The mechanical properties of the two alloys are similar (Table 9-7), and their corrosion resistance is similar to that of CP Ti. Their elastic moduli are similar to those of type 4 alloys, and yield strengths range from those of type 2 to type 5 metallic materials, as described in ISO 22674 (Table 9-2).

CRITICAL QUESTION

Why does the manipulation of titanium alloys differ so much from that for Co-Cr and Ni-Cr alloys?

Manipulation of Titanium Alloys

The surface of titanium castings after divestment must be ground and polished to remove surface porosity and the α case for optimal functionality of the final prosthesis. The machinability of titanium and its alloys is generally considered poor because of several inherent properties of titanium, such as high chemical reactivity, relatively low thermal conductivity, high strength at high temperature, and low modulus of elasticity.

To eliminate the effect of oxygen during the fabrication of titanium prostheses, CAD-CAM has been used to produce titanium-based fixed prosthesis frameworks.

CRITICAL QUESTION

How do alloys for all-metal prostheses differ from those required for metal-ceramic prostheses?

Alloys for Metal-Ceramic Prostheses

The chief objections to the use of *dental porcelain* as a restorative material are its low tensile strength and shear strength (Chapter 10, Mechanical Properties). A method of minimizing this disadvantage is to bond the porcelain directly to a cast alloy substructure made to fit the prepared tooth. The process requires building on the metal substrate a tooth form with ceramic powder held together by a binder and subjecting the entire assembly to a heating process called *sintering*. Sintering densifies the packed ceramic particles to a solid firmly bonded to the metal substrate. This system is referred to as the *porcelain-fused-to-metal* (PFM) design. The preferred descriptive term for this composite system is *metal-ceramic*, and the metal is called *metal-ceramic alloy*. In this section, the requirements of metals, some representative alloy systems, and issues associated with these alloys are discussed.

Requirements of Alloys for Metal-Ceramic Applications

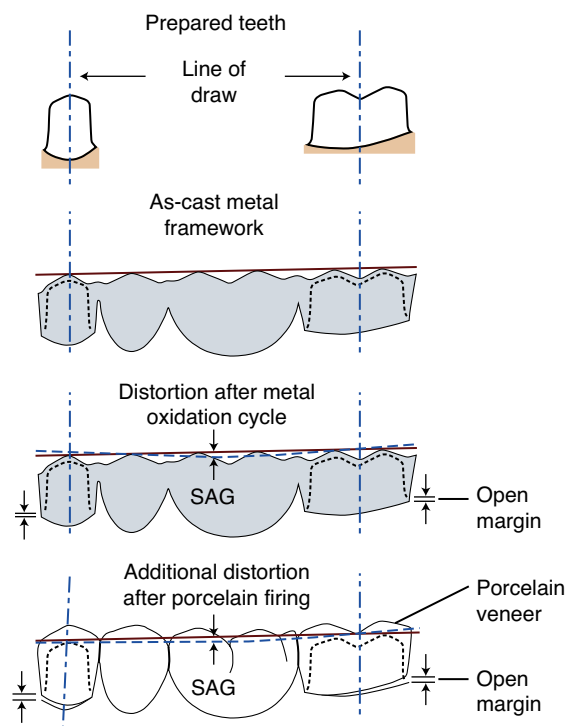
The alloys discussed in this section share at least three common features: (1) the potential to bond to dental porcelain, (2) solidus temperature sufficiently high to resist softening during sintering, and (3) coefficients of thermal contraction compatible with those of dental porcelain.

Porcelain Bonding to Metals

Porcelain bonding to metal substrate requires adherent oxides on the surface. The addition of a small quantity of an appropriate base metal to noble and high-noble alloys promotes oxide formation on the surface. For base-metal alloys, some oxides may be poorly adherent to the metal substructure, which can result in porcelain delaminating from the metal substrate. However, the bond strengths for porcelain bonded to base-metal alloys as determined *in vitro* have not generally been shown to be superior or inferior to those of noble-metal alloys. Furthermore, clinical studies have not demonstrated a significant difference in the failure incidence between metal-ceramic restorations made from base-metal alloys and those fabricated from high-noble or noble-metal alloys. To produce the optimal metal oxide characteristics, the manufacturer's instructions must be followed precisely.

Solidus Temperature

When an alloy is heated close to its solidus temperature, it becomes susceptible to deformation under its own mass, which is known as *creep*. The degree of creep increases with the size of the prosthesis and the number of firings required for the porcelain. In the older literature, this creep process is referred to as the *sag* of the ceramic alloy (Figure 9-2). All metal-ceramic alloys should have a solidus temperature that is substantially higher than the sintering temperature of the porcelain to minimize creep deformation.



• **Figure 9-2** Sag deformation in a fixed dental prosthesis (FDP) framework.

CRITICAL QUESTIONS

How can differences in thermal contraction between a metal and its veneering ceramic affect the resistance to cracking or fracture of the veneer? Why must a metal for metal-ceramic prostheses have its thermal contraction coefficient slightly higher than that of its veneering ceramic?

Thermal Compatibility of Metal-Ceramic Systems

The thermal expansion and contraction values of base-metal alloys are generally similar to those of noble-metal alloys. When a metal-ceramic prosthesis is cooled from the porcelain sintering temperature, the metal and its veneering ceramic contract at different rates. Meanwhile, the chemical bond between the metal and the porcelain prevents the two components from separating; this condition forces the two components to adjust their respective dimensions during the cooling cycle. Thus the component that contracts more will be stretched by the adjacent component, which contracts less; together, the material that contracts less will be compressed by the other component. Such changes in dimension result in stresses that act on each of the two components. The instantaneous stress at a given temperature during the cooling cycle is termed *transient stress*, and the stress distribution, which exists at room temperature, is called the *residual stress*. When the prosthesis is cooled, the tensile stress that develops in the porcelain is of concern. If the transient tensile stresses that develop within porcelain during cooling are insufficient to cause immediate cracking of the porcelain or delayed cracking after cooling to room temperature, the combination of a metal-porcelain system is considered thermally compatible. In fact, a slight thermal contraction mismatch, with a coefficient of thermal contraction of about $0.5 \times 10^{-6}/^{\circ}\text{C}$ higher for the metal, is preferred because the mismatch induces residual compressive stress in the porcelain along the bonded interface, which is protective in nature. This mechanism will be discussed in [Chapter 10, Coefficient of Thermal Expansion Mismatch](#).

CRITICAL QUESTION

What are the benefits and drawbacks of the different types of alloys used for metal-ceramic prostheses?

High-Noble and Noble Alloys

[Table 9-8](#) shows some typical high-noble and noble metal-ceramic alloys. The physical and mechanical properties of representative alloys are given in [Table 9-9](#).

Gold-Platinum-Palladium Alloys

Gold-platinum-palladium alloys produced the first successful metal-ceramic restorations. Platinum raises the melting temperature. Rhenium (Re) is a grain refiner that increases hardness. Iron forms an oxide on the surface for porcelain bonding and increases the proportional limit and strength of the alloy by an FePt_3 precipitate. These alloys have adequate elastic modulus, strength, hardness, and elongation but are low in sag resistance. They are mostly used for making crowns and three-unit FDPs. Their use has decreased over time because more economical alloys have been developed with substantially better mechanical properties.

Gold-Palladium-Silver Alloys

Gold-palladium-silver alloys are economical alternatives to the Au-Pt-Pd or Au-Pd-Pt alloys. Their excellent tarnish and corrosion resistance and relative freedom from technique sensitivity have contributed to their long-term success. The higher palladium concentration above those of the Au-Pt-Pd alloys raises the melting ranges and improves resistance to creep deformation at elevated temperatures.

Gold-Palladium Alloys

These silver-free alloys are white in color and have a lower thermal contraction coefficient than that of either the Au-Pd-Ag or Pd-Ag alloys. When used with compatible low-expansion or low-contraction porcelains, Au-Pd alloys are considered nearly ideal compared with other noble-metal alloys because these alloys contain no silver, and their surface oxide is virtually indiscernible. Thus the esthetic quality of metal-ceramic prostheses made with Au-Pd alloys is comparable to that obtained with Au-Pt-Pd alloys. The sag resistance of these alloys is somewhat better than that of Au-Pt-Pd alloys.

Palladium-Gold Alloys

The physical properties of palladium-gold alloys are generally similar to those of the Au-Pd alloys, and potential thermal contraction concerns for these alloys seem to have been resolved by changes in the porcelain composition. Few data are available on their laboratory and clinical performance.

Palladium-Gold-Silver Alloys

Palladium-gold-silver alloys are similar to the Au-Pd-Ag alloys in their potential for porcelain discoloration. They have a range of thermal contraction coefficients, which increase with an increase in silver content.

Palladium-Silver Alloys

This alloy type was the first gold-free noble alloy for metal-ceramic restorations. The replacement of gold by palladium raises the melting range but lowers the thermal expansion coefficient of the alloy. Silver, on the other hand, lowers the melting range but increases

TABLE 9-8 Compositions of Representative High-Noble (HN) and Noble (N) Alloys for Metal-Ceramic Prostheses

Alloy Type	Typical Products (Supplier)	PRINCIPAL ELEMENTS (WEIGHT PERCENT)						
		Au	Pt	Pd	Ag	Cu	Ga	Balance*
Au-Pd-Pt/HN Au-Pt-Pd/HN Au-Pt-Ag/HN	SMG-3 (Dentsply Ceramco) [†]	81	6	11	—*	—	—	Re; Sn; Fe
	Argedent Y86 (Argen) [†]	86	10	2	—	—	—	In:2
	Degunorm (Dentsply Ceramco) [†]	74	9	—	9	4.4	—	Zn; In; Ir
Au-Pd-Ag/HN	Argedent 75 (Argen) [†]	75	—	12	10	—	—	In:1; Sn:1; Ir
	Aspire (Dentsply Ceramco)	52	—	26	17	—	—	Zn; In; Sn; Re
	Herabond (Heraeus-Kulzer)	52	—	27	18	0.2	—	Sn:2.7; In; Ir; Re
Au-Pd/HN	Olympia (Argen)	52	—	38	—	—	1.5	In:8.5; Ru
	Lodestar (Ivoclar Vivadent)	52	—	39	—	—	1.5	In:8.5; Re; Ru
	Argedent 65SF (Argen)	65	—	26	—	—	—	In:8.7
Pd-Au/N	Argedent 35SF (Argen)	35	—	57	—	—	4.8	Sn:3; Zn; Ru
Pd-Au-Ag/N	Argelite 52+ (Argen)	15	—	52.2	21.5	—	1	In:6; Sn:4
	Argelite 75+6 (Argen)	6	—	75	6.5	—	—	In:6; Ga:6
Pd-Ag/N	Albabond A (Heraeus-Kulzer)	—	—	57	33	—	—	Sn:6.8; In:3.4; Zn; Ir; Ru
	W-1 (Ivoclar Vivadent)	—	—	53	38	—	—	Sn:8.5; In; Ru; Li
Pd-Cu-Ga/N	Spartan Plus (Ivoclar Vivadent)	2	—	78.8	—	10	9	Ir; Ge; Li
Pd-Ga/N	Argebond 80 (Argen)	—	—	80	5	—	6.3	In:6.5; Sn; Zn:1
	Argelite 85 (Argen)	2	—	85	1.2	—	10	In:1.2; Ru

*Elements without value are less than 1% by weight.

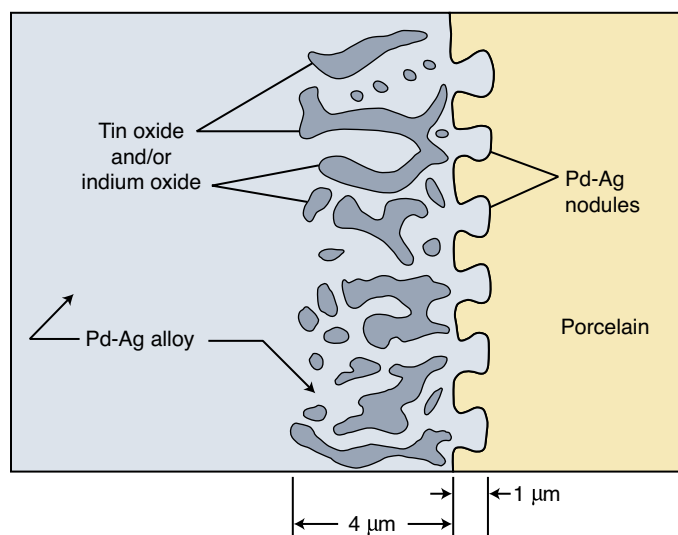
[†]Yellow-color alloy.**TABLE 9-9 Physical and Mechanical Properties of Some High-Noble and Noble Metal–Ceramic Alloys in Table 9-8**

Alloy Type	Product Name	Density (g/cm ³)	Yield Strength (MPa; Soft/Hard)	Hardness (VHN; Soft/Hard)	Elastic Modulus (GPa)	Elongation (Soft/Hard) (%)
Au-Pt-Ag	Argedent Y86	18.4	405/469	160/195	76	12/9
Au-Pd-Ag	Herabond	14.5	520/600	220/260	134	12/8
Au-Pd	Olympia	14.4	550	250	124	30
Pd-Au	Argedent 35SF	13.9	510/572	245/245	124	25/20
Pd-Au-Ag	Argelite 75+6	11.4	565/600	250/265	111	32/30
Pd-Ag	Albabond A	11.4	460/540	205/235	122	26/18
Pd-Cu-Ga	Spartan Plus	11.0	740	310	140	10
Pd-Ga	Argebond 80	11.2	585/630	230/245	130	35/28

VHN, Vickers hardness number.

the thermal expansion coefficient. A proper balance of the two elements maintains a reasonably low casting temperature and a compatible thermal expansion coefficient. The thermal compatibility of these alloys is generally good except with certain low-expansion porcelains. The addition of tin and indium promotes oxide formation for porcelain bonding and yields precipitates for improving mechanical properties.

Adherence to porcelain is considered acceptable for most of the Pd-Ag alloys. However, Mackert et al. reported that one of these alloy products formed an internal oxide rather than the preferred external oxide. Instead, Pd-Ag nodules developed on the surface (Figure 9-3) facilitate the retention of porcelain mechanically. This condition has not apparently produced clinical bond failures to warrant concern, and other Pd-Ag ceramic alloys have



• **Figure 9-3** Internal oxide formation and creep-induced nodule formation in a Pd-Ag alloy for metal-ceramic restorations.

not been studied to determine whether they have similar oxidation behavior.

Because of their high silver content compared with that of gold-based alloys, the potential silver discoloration effect is most severe for these alloys. One should proceed with caution when light shades (higher values) of ceramic are desired.

Palladium-Copper-Gallium Alloys

Compositional differences for the Pd-Cu-Ga alloys result in a wide range of mechanical properties: yield strengths ranging from 520 MPa to over 1200 MPa, percent elongation ranging from 7% to 30%, and VHN ranging from approximately 265 to over 400. Careful composition control by manufacturers has resulted in Pd-Cu-Ga alloys with VHNs of substantially less than 300.

The dark brown or black oxide formed during oxidation and subsequent porcelain sintering cycles makes it difficult for a technician to mask the color. Sometimes a thicker opaque porcelain layer is required to avoid excessive darkness (i.e., low value) with certain porcelains. An increase in oxide-layer thickness occurs during the initial oxidation step for these alloys. To reduce the discoloration effect, the surface can be sandblasted prior to the application of opaque porcelain.

Palladium-Gallium Alloys

The Pd-Ga alloys also have relatively dark oxides, which are somewhat lighter than those on the Pd-Cu-Ga alloys. Pd-Ga alloys generally tend to have relatively low thermal expansion coefficients, making the alloys more compatible with lower-expansion porcelains. The silver content is generally low and is not sufficient to cause significant porcelain “greening.”

The effects of several dental laboratory variables (recasting old alloy, alternative oxidation cycle, stripping and rebonding of porcelain) on porcelain adherence were investigated for one Pd-Ga alloy, three Pd-Cu-Ga alloys, and one Au-Pd alloy. One finding was that remelting two and three times degraded porcelain adherence to the Pd-Ga alloy and one Pd-Cu-Ga alloy. Stripping of the original porcelain did not cause a significant decrease in adherence of the subsequently applied porcelain. An alternate oxidation procedure from the one recommended by the manufacturer significantly affected porcelain adherence to one Pd-Cu-Ga alloy and the Au-Pd alloy. Therefore where there is doubt, the manufacturer should be

asked to provide precise instructions to ensure sound metal-ceramic bonding.

CRITICAL QUESTION

What are the benefits and drawbacks of using a base-metal casting alloy versus a noble-metal casting alloy for a metal-ceramic restoration?

Predominantly Base-Metal Alloys

Compared with other alloys for metal-ceramic prostheses, the base-metal alloys (other than titanium and titanium alloys) generally are harder and stiffer (higher elastic modulus) (Tables 9-4 and 9-5); this enables the coping to be 0.1 to 0.2 mm thick without risking significant deformation under mastication stress or sagging of the metal framework at the porcelain-firing temperature. The higher melting temperatures make these alloys more difficult to cast than the high-noble and noble alloys.

Manipulation of Base-Metal Alloys

Laboratory technicians fabricating base-metal copings for metal-ceramic prostheses will face the following technical issues: casting condition, castability, finishing, and controlling oxide layers. The fusion temperatures of Ni-Cr and Co-Cr alloys are in the range of 1150 to 1500 °C; an acetylene-oxygen flame or an electrical induction heating source is required for melting these alloys. The mold should be made of either phosphate- or silicate-bonded investment material, which maintains its surface integrity at the casting temperature of base-metal alloys. The density of a base-metal alloy is about half that of a gold-based alloy. The lower density reduces the force of gravity for bulky maxillary appliances on the supporting teeth but also reduces the thrust generated by the casting unit to force the molten base-metal alloy to fill the mold. The use of a vent and a larger sprue size than that used for gold-based alloys may be needed (Chapter 14, Wax Pattern and Sprue Design).

The castability of Co-Cr alloys is in the same range as that of Ni-Cr alloys without beryllium. Some noble and high-noble alloys were found to exhibit lower castability than Co-Cr alloys. In contrast, a study of the marginal accuracy of a high-noble alloy, four noble alloys, and a Ni-Cr-Be alloy revealed that for all alloys, marginal completeness was adequate, and marginal openings were considerably less than 50 μm. Some researchers claim that all alloys will theoretically produce complete castings under optimal burnout, melting, and casting conditions.

In general, the high hardness and high strength of these base-metal alloys contribute to certain difficulties of adjusting prostheses. After casting, it is useful to sandblast the prosthesis to remove investment materials and excessive oxides. Grinding and polishing of fixed restorations to achieve proper occlusion will occasionally require more time at chairside. The removal of defective restorations may also require more time. The potential hazard of dust generated from the procedure is a concern and is discussed with the biological hazards of base-metal alloys (Chapter 17, Dental Alloys).

The solidification shrinkages of base-metal alloys are greater than those of gold-based alloys, which represents a challenge for technicians to obtain acceptable-fitting base-metal castings. Using type V die stone for dies and enhancing the expansion of the investment mold during the setting of the investment are the most common practices to improve the fit of prostheses (Chapter 14, Control of Shrinkage Compensation).

The thickness of the oxide layer and the wetting of the oxide layer by porcelain are important factors in establishing the bonding

of porcelain to the metal substrate. For the laboratory technician to produce optimal metal-oxide characteristics, the manufacturer's instructions must be followed precisely. However, some instructions are relatively imprecise. For example, some alloys require a "light" sandblasting of the oxide layer formed during the initial oxidation step. The particle size of aluminum oxide abrasive is generally recommended, but neither the quality of abrasive nor the sandblasting pressure is usually specified. Contamination of the oxide layer with lower-purity abrasives could degrade the integrity of the interface between the metal oxide and the opaque porcelain. The ability of a laboratory technician to discriminate light from moderate sandblasting to reduce the thickness of these surface oxides is one example of the technique sensitivity of base-metal alloys.

Mechanical Properties

The elastic modulus of base-metal alloys is twice as much or greater than those for noble-metal alloys. This property allows the technician to reduce the cross-sectional area of cast interproximal connectors. The rigidity of the prosthesis is proportional to the elastic modulus and the connector width (buccal-lingual dimension) but is proportional to the cube of the connector thickness (occlusal-gingival dimension). The cubic relationship with the connector thickness means that when an alloy with an elastic modulus that is twice as high is used, the connector thickness can be reduced by 20.6%, while maintaining the same rigidity of the prosthesis. Using similar reasoning, a reduction of the coping thickness from 0.3 to 0.1 mm may increase the risk of porcelain fracture because of the increased coping flexibility. However, a finite-element analysis of stresses induced in anterior metal-ceramic crowns under intraoral forces indicates that a reduction of base-metal coping thickness (in veneered areas) from 0.3 to 0.1 mm exhibits only a slight effect on porcelain stresses.

It is a common practice to design the occlusal surface of metal-ceramic prostheses to be made from cast metal to avoid excessive wear of the opposing natural dentition. Compared with the same prostheses made of high-noble or noble alloys, the hardness of the base-metal alloys makes the occlusal adjustment slightly more difficult to perform, and the resulting roughness can cause greater wear of the opposing tooth enamel. Repair of crowns with fractured porcelain veneers, which may be simply performed on noble-metal substrates using pin-retained facings or metal-ceramic onlays, is more difficult to accomplish when the failed restoration has a framework cast with a nickel- or cobalt-based alloy.

Titanium-Based Alloys

As previously discussed, titanium undergoes a phase transformation at 882 °C and exhibits a high rate of oxidation above 900 °C. Therefore a low-fusing ceramic with a sintering temperature below 800 °C should be used to minimize oxidation and prevent any phase transformation during sintering. The high melting temperatures of CP Ti and titanium alloys makes them highly resistant to sag deformation at porcelain-sintering temperatures, and the accompanying relatively low thermal expansion coefficient demands special low-expansion dental porcelains for bonding to titanium. Because of the α -case formation, caustic NaOH-based solutions or silicon nitride coatings have been employed to improve the bond between cast CP Ti and dental porcelain.

In general, in vitro bonding tests show that metal-ceramics fabricated from noble and base-metal alloys exhibit higher bond strengths than those of low-fusing porcelain to titanium. However, a small number of studies show that the bond strengths are not statistically significantly different between the two groups. Differences in porcelain composition often require different firing temperatures, which may result in bond-strength changes. However, there is no difference in porcelain bond strength between CP Ti and titanium alloys. Studies also show that surface treatment of CP Ti and titanium alloy before porcelain application can improve the bond strength. The treatments include silica deposition by magnetron sputtering; deposition of an intermediate metallic layer by silver plating; use of an admixture of titanium particles and porcelain as a bonding agent; incorporation of an intermediate ceramic layer; nitridation of the titanium surface; and surface roughening by a caustic bath, hydrochloric acid, or sandblasting. Although multiple firing has no effect on bond strength, firing in an argon atmosphere, which reduces oxide formation, improves the bond strength. It is believed that controlling the thickness and adherence of the oxide is the key to higher bond strength.

Properties of high-noble and base-metal alloys (including CP Ti) for metal-ceramic prostheses are listed in [Table 9-10](#).

CRITICAL QUESTION

Which factors must be considered by the dental laboratory and dentist for the preparation and adjustment of RPD frameworks that are cast from base-metal alloys?

TABLE 9-10 Comparative Properties of High-Noble Alloys and Base-Metal Alloys for Metal-Ceramic Prostheses

Property	High-Noble Alloy	Co-Cr	Ni-Cr-Be	CP Ti
Biocompatibility	Excellent	Excellent	Fair	Excellent
Density	14 g/cm ³	7.5 g/cm ³	8.7 g/cm ³	4.5 g/cm ³
Elastic modulus (stiffness)	90 GPa	145–220 GPa	207 GPa	103 GPa
Sag resistance	Poor to excellent	Excellent	Excellent	Good
Technique sensitivity	Minimal	Moderately high	Moderately high	Extremely high
Bond to porcelain	Excellent	Fair	Good to excellent	Fair
Metal cost	High	Low	Low	Low*

*The dental laboratory costs for fabricating metal-ceramic prostheses are high for CP Ti, and few dental laboratories have the capability of producing Ti prostheses.

TABLE 9-11 Compositions and Mechanical Properties of Selected Base-Metal Alloys for Removable Partial Dentures*

Alloy Name (Supplier)	ELEMENTAL COMPOSITION (WEIGHT PERCENT)					MECHANICAL PROPERTIES			
	Ni	Co	Cr	Mo	Balance*	Yield Strength (MPa)	Hardness (VHN)	Elastic Modulus (GPa)	Elongation (%)
Nobilstar (CMP Industries)	—	65	27.5	5.5	Si; Fe; Mn; C	640	430	193	9
Vitallium (Dentsply)	—	63.1	28.5	6	Mn; Si; C; N	600	410	200	9
JD (Jelenko Alloys/Argen)	—	63	28.5	6	Si; C; Mn; Fe; W	620	290	207	5
Heraenium EH (Heraeus Kulzer)	—	63.5	28	6.5	Si:1; Mn; C; N	620	310	228	7
Suprachrome+ (Argen)	—	63	30	5	Mn; Si; C; N	745	390	200	13
Supercast (Pentron Alloys/Argen)	—	64	30	4	Mn; Si; C; N	655	340	228	3.5
Ticonium 100 (CMP Industries)	71.6	x†	16	5	Al: 2.9; Mn: 3.7 Be: 0.8; Ti	790	360	186	7

VHN, Vickers hardness number.

*Elements without value are less than 1% by weight.

†x indicates trace amount.

Alloys for Removable Partial Dentures

RPDs have four major metal components: connectors, rests, clasps, and mesh bases. Except for clasps, each component should be rigid and resist permanent deformation, which suggests a material of high elastic modulus and yield strength. Table 9-11 lists the compositions and mechanical properties of selected base-metal alloys for RPDs. The density of these alloys ranges from 7.6 to 8.3 g/cm³. For clasps, the material must be resistant to permanent deformation, flexible to engage undercuts, and possess sufficient ductility to facilitate adjustment without fracture. Ideally, the clasps should be made of gold-based type 4 alloy because of its lower elastic modulus, good ductility, and adequate yield strength (Table 9-4), and then soldered (discussed later) to the remaining framework made of a base-metal alloy. This arrangement, however, inevitably promotes corrosion at the soldered (braze) joint (Chapter 3, Dissimilar Metals). Although gold-based clasps can be embedded in the denture base resin to avoid corrosion at the solder joint, in practice, RPDs are cast in one piece using the same alloy. The effect of the high elastic modulus of the base-metal alloy on the flexure and retention of the clasps can be adequately addressed by reducing the clasp thickness. The situation is similar to that discussed for FDPs.

Predominantly Base-Metal Alloys

Cobalt-chromium-molybdenum alloy has been the primary metal for RPD prostheses. Cobalt increases the elastic modulus and strength. Inclusion of greater than 30% chromium by weight makes the alloy difficult to cast and forms the brittle σ phase. Molybdenum and manganese improve the corrosion resistance of the alloy. Carbide formation provides a high yield strength and

hardness in the alloy but lowers ductility. Particular concerns are the higher hardness of some alloys, which can cause in vivo wear of the enamel; the need for special finishing in the dental laboratory; and the tendency of these alloys to undergo rapid work hardening.

Co-Cr alloy clasps are reported to be too retentive initially and to slowly lose this retention because of permanent deformation from repeated seating and removal of the appliance, which correspond to cyclic fatigue conditions. Caution is needed by the dental laboratory technician or the clinician in adjusting clasps on the cast framework to avoid fracture, even for RPD alloys that exhibit higher values of percent elongation.

Because of the high melting temperatures, these base-metal alloys are induction-melted and cast using phosphate- or silicate-bonded investments, as recommended by the manufacturer, to compensate for their high casting shrinkage and to minimize the potential for casting defects.

CRITICAL QUESTION

Because titanium alloy has an elastic modulus comparable to that of gold, how can the stiffness of an RPD made from this titanium alloy be increased to the same level of stiffness as a cobalt-chromium RPD?

Titanium-Based Alloys

CP Ti and titanium alloys have occasionally been used to make RPD frameworks because of the excellent biocompatibility, outstanding corrosion resistance, and good mechanical properties. Because of the low elastic modulus, compared with that of base-metal alloys, the rigidity of the connector is often improved by increasing the thickness or changing the design. Increasing the rigidity also reduces debonding between the resin base and the

metal framework. In addition, the lower yield strength and higher percent elongation of CP Ti suggest that cast clasps may be easily adjusted.

Laboratory casting of titanium remains a challenge because internal porosity within the clasp assemblies can lead to clasp fracture. The reaction layer on the surface must be removed chemically with hydrofluorosilicic acid or mechanically by sandblasting and rotary instruments.

The strong binding and high electrostatic character of the titanium surface oxide may result in higher plaque adherence to titanium frameworks compared with other base-metal frameworks. A clinical survey of RPDs revealed gradual discoloration of titanium alloy frameworks, whereas those made with CP Ti and other base-metal alloys did not discolor. It was hypothesized that aluminum segregates from the titanium alloy (Ti-6Al-4V) during casting and corrodes during service; further research is needed to verify this hypothesis. An in vitro study has also revealed that exposing titanium alloys to alkaline denture cleansers (pH greater than 11) causes discoloration. Laser **welding** of titanium has facilitated the repair of titanium frameworks because of the low thermal conductivity of titanium and localized heating during laser welding. This is also true for the Co-Cr and Ni-Cr alloys.

CRITICAL QUESTION

What are the merits and concerns of using alternative techniques other than casting for fabricating prostheses from dental alloys?

Alternative Technologies for Fabricating Prostheses

Shrinkage of the dental casting alloy in an investment mold occurs in three stages: (1) the thermal contraction of the liquid metal cooling to its liquidus temperature (Figure 2-17), (2) the phase change from the liquid to the solid state (solidus temperature), and (3) the thermal contraction of the solid metal from the solidus temperature to room temperature (Figure 2-17). The linear solidification shrinkage of an alloy resulting from thermal contraction differs from the casting shrinkage for dental alloys because of the effect of the investment surrounding the solidifying casting.

The first-stage contraction is of no consequence to the final dimensions of the casting because the molten metal flows freely and fills the mold. For the second-stage contraction, the solidification starts at the walls of the mold, and the first layer of metal tends to adhere to the mold, while the liquid metal continues to be fed from the reservoir, which results in no contraction of the casting relative to the investment mold. As the casting cools, it gains sufficient strength to contract independently of the mold. Any contraction of the casting from this point will affect the fit of the prosthesis. Finally, the casting shrinks thermally until it reaches room temperature. Because the thermal contraction coefficient of the metal casting is higher than that of the investment mold, the size of the final casting will be smaller than that of the investment mold, which is an accurate reproduction of the missing tooth structure. The difference in dimensions is called *casting shrinkage* and normally is compensated for by the setting and thermal expansion of the investment used (Chapter 14, Investment Materials). Table 9-12 lists the linear solidification shrinkage of various alloys cast as smooth cylinders. Because the contraction of the alloy as it cools to room temperature dominates the casting shrinkage, the higher-melting alloys tend to exhibit greater shrinkage.

TABLE 9-12 Linear Solidification Shrinkage of Casting Alloys

Alloy Type	Casting Shrinkage (%)
Type 1 (Au-based)	1.56
Type 2 (Au-based)	1.37
Type 3 (Au-based)	1.42
Type 4 (Ni-Cr-based)	2.30
Type 4 (Co-Cr-based)	2.30

Technologies are currently available for fabricating metallic prostheses without metal melting and the associated casting shrinkage. Except for RPD frameworks, most metal prostheses can be made by one or more of the following methods: (1) sintering (or diffusion bonding) of burnished metal foil, (2) CAD-CAM processing of metal blocks, (3) copy milling of metal blocks, and (4) electroforming of metal copings. A fifth method, which has become highly popular worldwide, 3-D printing with selective laser melting of metal powder, can be used to fabricate most metal prostheses, including RPD frameworks.

Sintering of Burnished Foil

The most commonly used commercial foil system, Captek (Leach & Dillon, North Attleboro, MA), is used for making copings or frameworks for metal-ceramic prostheses. The protocol and guidelines for the Captek system are found in an article in the Selected Readings section. The main advantage of Captek crowns is their very low thickness, which ensures minimal tooth reduction or improved esthetics compared with conventional metal-ceramic crowns made with cast metal copings. For the construction of a multiple-unit FDP, a connector for the two abutment copings is waxed and cast with a recommended gold alloy. The copings are then joined with the connector using furnace soldering, electrical welding, or laser welding before the porcelain application.

CAD-CAM Processing

The dental application of CAD-CAM became available in the early 1980s to produce ceramic inlays and crowns during one chairside appointment. This technology has been improved and expanded, and computer-aided milling or grinding of a metal or a ceramic block can be performed accurately by a CAD-CAM process or by electrolytic or electrical discharge removal of metal. The CAD-CAM technique can be used to prepare prostheses from CP Ti or titanium alloy, which do not contain bulk casting defects or the hard α case found near the surface of cast titanium prostheses. More about the CAD-CAM process is provided in Chapter 15, Prototyping Tools.

Copy Milling

The copy-milling process is based on the principle of tracing the surface of a resin prosthesis pattern, which is then replicated on a blank of ceramic, composite, or metal that is ground, cut, or milled by a rotating wheel whose motion is controlled by a link through the tracing device. The process is similar to that associated with cutting a key blank using a tracing of a master key. One commercial system of this type (Celay, Mikrona Technologies, Spreitenbach, Switzerland) has been in use since 1991. The pattern

to be traced is made from a blue-colored, resin-based composite (Celay-Tech, ESPE, Seefeld/Oberbayern, Germany).

Electroforming

A master cast of the prepared tooth (teeth) is prepared and coated with a special die spacer to facilitate separation of the duplicating material. The dies are duplicated with a gypsum product that has a setting expansion of 0.1% to 0.2%. After a conductive silver layer is applied to its surface, the die is connected to a plating head, and then to a power source and placed in a plating solution. After a sufficiently thick layer of gold or other metal is deposited, the gypsum is removed, and the coping is sandblasted. The coping is then coated with a bonding agent during the wash bake, and subsequent ceramic layers are condensed and sintered in a conventional way.

As is true for the burnished foil system, a cast pontic is needed for joining electroformed copings to construct multiple-unit prostheses.

Three-Dimensional Printing

The process of 3-D printing is a form of additive manufacturing technology where a 3-D object is created by depositing successive layers of material. This technology is now being widely used with metal powders to fabricate dental restorations and prostheses. As described in [Chapter 15, Additive Manufacturing—3D Printing](#), the metal powder is first spread across the working platform. A laser traces the outline of each part being printed, and metal powder is fused to the layer below it. As the platform is lowered, a new layer of material is spread across the platform, and the process is repeated until the printing process is completed. This process is called *selective laser melting* or *direct laser metal sintering*. For dental applications, the metal powder can be titanium, Co-Cr alloy, or a noble metal. The powder compositions for two Co-Cr alloys used for selective laser melting are shown in [Table 9-13](#), and it can be seen that these powder compositions are very similar to the compositions of the base-metal casting alloys shown in [Table 9-11](#). Additional technologies are discussed in [Chapter 15, Prototyping Tools](#).

Örtorp et al. reported the marginal and internal fit among three-unit Co-Cr-based FDPs using four fabrication techniques: (1) the traditional lost wax casting method, (2) CAD-CAM milling of a wax pattern followed by the lost wax casting method, (3)

the CAD-CAM milling method, and (4) the direct laser metal sintering method. Initial results indicate that the best fit was exhibited by group 4, followed by groups 2, 1, and 3. A review published in 2020 shows that the total gap of single-crown soft milling had the highest accuracy, and for multi-unit FDPs, additive manufactured restorations had the highest accuracy.

CRITICAL QUESTION

What are the differences between soldering, brazing, and welding?

Joining of Dental Alloys

There are three categories of metal-joining operations: soldering, brazing, and welding. The soldering and brazing processes for the metallic components (also called *substrate metals*) to be joined always employ a *filler metal* (usually called *solder*), along with a **flux** and a heat source. Brazing is conducted above 450 °C, and soldering is conducted below that temperature. Both processes are performed below the solidus temperature of the substrate metal or metals; there is no melting at the workpiece surfaces. The term *soldering* is used in this section as a general term to describe both processes. Welding may not require a filler metal because the metal surfaces to be joined melt and fuse locally. The common characteristic of these operations is the achievement of bonding between the workpieces and/or the filler metals by a controlled heating procedure.

Metal-joining processes in dentistry have traditionally been dominated by the gold-based alloys, and soldering (or brazing) using a flame torch has been the main process. With the newer nongold alloys, the requirements of the metal-joining process differ among the alloys used. For example, titanium alloys oxidize readily at elevated temperatures, and an oxygen-free environment and a nonoxygen heating source are needed.

Spot welding based on electrical resistance has been used to weld alloys of low thermal conductivity, such as orthodontic appliances. New advances in the technology of heating sources have been adapted for orthodontic and other dental applications. They include the plasma torch, Nd:YAG laser, and tungsten-inert gas (TIG) arc. The advantages of these technologies are that the area of heating is small—it can be 0.2 mm with the laser and TIG—and the duration of heating can be controlled. When the area of heating is very small, the thermal conductivity of the alloy can be of concern. High thermal conduction dissipates the thermal energy needed for melting the substrate metal. The very small area of heating is advantageous for Co-Cr and titanium alloys, which have lower thermal conductivities than gold-based alloys.

Although the advantages of modern heating sources have shifted the operation of metal joining in dental laboratories toward welding, gold soldering is a simpler procedure that can be conducted in the dental office.

CRITICAL QUESTION

Why should the flow of flux be restricted, and what kind of material is used?

Soldering Flux

A metal surface free of any contaminant, such as oxides, is essential for establishing metallic bonds between substrate metals. A flux is needed, and it has three primary functions: (1) dissolve surface oxides, (2) reduce existing oxides to pure elements, and (3)

TABLE 9-13 Powder Compositions for Two Co-Cr Alloys Used for Selective Laser Melting

Manufacturer	Co	Cr	Mo	Si	Mn	Fe
SINT-TECH, France ¹	Balance (max. 62.5)	29	5.5	<1	<1	<1
Epson Atmix, Japan ²	Balance (approx. 63.5)	29	6	<1	<1	<1

¹Al Jabbari YS, Barmpagadaki X, Psarris I, Zinelis S: Microstructural, mechanical, ionic release and tarnish resistance characterization of porcelain fused to metal Co-Cr alloys manufactured via casting and three different CAD/CAM techniques, *J Prosthodont Res*. 63:150–156, 2019.

²Takaichi A, Suyalatu, Nakamoto T, et al: Microstructures and mechanical properties of Co-29Cr-6Mo alloy fabricated by selective laser melting process for dental applications, *J Mech Behav Biomed Mater*. 21:67–76, 2013.

protect the surface from oxidation during soldering. The solder chosen must wet the metal substrate to be joined. To prevent the flow of molten solder onto adjacent areas, an **antiflux**, such as rouge mixed with chloroform or graphite, can be painted on these areas before heating the substrate metals.

Fluxes for use with noble-metal alloys are generally based on boric acid, boric anhydride, and borax. Chromium oxides that form on base-metal alloys are more stable, and fluoride-containing fluxes are needed to dissolve chromium, nickel, and cobalt oxides. Fluxes are also available for different temperature ranges to provide optimal activity.

The amount of flux used should be minimized because entrapment of flux within the filler metal can cause a weakened joint. Residual flux that is covered with porcelain can cause discoloration and bubbling of the porcelain. Flux combines with metal oxides and forms a glass during the soldering process, and the residue should be removed. After the soldering process, sandblasting the joint with alumina abrasive particles immediately after removal from the soldering investment and boiling in water are needed to remove glassy residue resulting from the reaction between the flux and oxides.

Filler Metal for Soldering

The filler metals should have acceptable color, adequate hardness and strength, and tarnish and corrosion resistance relative to the workpieces. Fillers and substrates do not need to have similar compositions, but the filler metals should have (1) a sufficiently low flow temperature, (2) the ability to wet the substrate metal, and (3) sufficient fluidity at the flow temperature.

Flow Temperature

When the filler metal melts, wets, and flows on the substrate metal, it bonds to this workpiece. The flow temperature of the filler metal is usually higher than its liquidus temperature to provide suitable viscosity and must be sufficiently lower than the solidus temperature of the substrate metal that melting of the substrate does not occur. For an alloy substrate that will be veneered with porcelain after soldering, the melting range of the filler metal should be higher than the sintering temperature of the porcelain to avoid sag deformation of the bridge framework during subsequent porcelain firing.

Wetting

Recall the discussion of the role of wetting in [Chapter 2, Wetting](#). Wetting of the substrate metal by the molten filler metal is essential to produce a metallic bond. Oxides have poor wettability characteristics; therefore molten metal does not spread on the oxide layer of substrate metals. That is the reason why iron oxide is used as antiflux.

Fluidity

Molten filler metals should flow freely into the gap between the two substrate metals. When the surface of a metal prosthesis needs to be extended, such as for a deficient interproximal contact area, a filler metal can be used to build up the area. A filler metal with relatively sluggish fluidity then becomes desirable. This type of filler usually has a wide melting range, and flow can be controlled to well-defined areas.

CRITICAL QUESTION

How can one best assess if the quality of a solder joint is acceptable or not?

TABLE 9-14 Thermal Characteristics of Fuel-Gas Combustion

Fuel	Flame Temperature (°C)	Heat Content (kcal/m ³)
Hydrogen	2,660	2,362
Natural gas	2,680	8,898
Propane	2,850	21,221
Acetylene	3,140	12,884

Heat Sources for Soldering

The most common instrument for the application of heat is a gas-air or gas-oxygen torch. All gases shown in [Table 9-14](#) have potential flame temperatures high enough to melt any dental casting alloy currently in use. The thermal energy (heat content measured in calories per cubic meter of the fuel) from the combustion of the fuel must not only raise the temperature of both the substrate metal and the filler metal to the soldering temperature but also compensate for heat loss to the surroundings. Fuel with a lower heat content requires a longer period of heating at the desired temperature and is associated with an increased danger of oxidation during the soldering process.

Of the fuel gases in [Table 9-14](#), the best choice is propane. Butane, which is more readily available in some parts of the world, has a similar flame temperature and heat content as propane. Both propane and butane have the advantage of being relatively pure compounds; therefore they are uniform in quality, are virtually water-free, and burn cleanly (provided that the torch flame is properly adjusted). With acetylene, which should only be used by an experienced dental laboratory technician, concerns are localized variations in flame temperature and the tendency for decomposition into carbon and hydrogen, with the incorporation of carbon in both nickel and palladium solders degrading the mechanical properties of the joints.

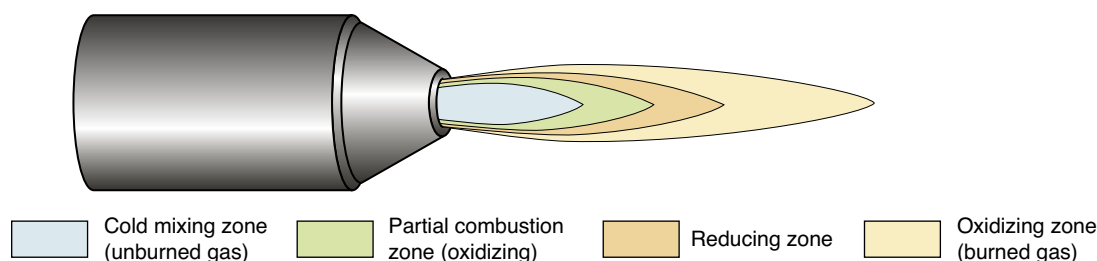
Another source of heating is a furnace that heats the assembled substrate metals along with flux and solder deposited at the joining site to an appropriate temperature for melting and flow of solder. Before the assembled substrate metals are placed into the oven, a uniform coating of a paste flux should be applied to the surface to be soldered. The advantage of furnace soldering is that every component can be heated and cooled uniformly in accordance with a precise schedule that prevents distortion, which might occur under localized heating, such as during soldering of metal-ceramic bridges.

CRITICAL QUESTIONS

Which type of torch gas should be used for soldering noble alloys? Why is it not possible to use all torch gases?

Technique Considerations for Soldering

For fixed prostheses, where accurate alignment is needed, investment soldering is used, in which the parts to be joined are first indexed and joined by a temporary material, such as acrylic resin or sticky wax, and then mounted in a soldering investment, which holds the parts together during the soldering procedure. In contrast, freehand soldering is used for assembling orthodontic and



• **Figure 9-4** Flame zones in a propane-oxygen torch flame.

some other appliances, in which the parts to be joined are manually held in contact during the soldering procedure. As soon as the filler metal has flowed to the desired position, the heating is discontinued, and the appliance is cooled.

The investment soldering technique involves several critical steps: (1) cleaning and preparing the surfaces to be joined, (2) assembling the parts to be joined, (3) preparation and fluxing of the gap surfaces between the parts, (4) maintaining the proper position of the parts during the procedure, (5) control of the proper temperature, and (6) control of the time to ensure adequate flow of solder and complete filling of the solder joint. Many of these steps are applicable to freehand soldering.

Other factors that may influence the result of soldering are discussed next.

Gap Width

The gap between the parts of the substrate metal to be joined must be sufficient to allow solder flow between the workpieces. If the gap is too great, the joint strength will be dictated by the strength of the filler metal. If the gap is too narrow, flux inclusions and porosity caused by incomplete flow of the filler metal may occur and lead to decreased strength. Inclusions or porosity can lead to distortion if any heating, such as porcelain application, takes place after the soldering operation. The ideal gap width is about 0.13 mm.

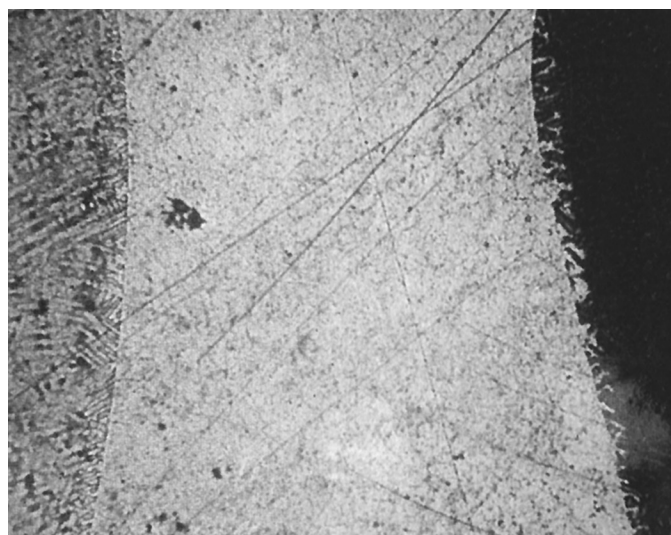
Flame

A torch flame can be divided into four zones, as shown in Figure 9-4. The portion of the flame used to heat the soldering assembly should be the tip of the reducing zone, in which the most efficient burning process occurs and the most heat is generated. An improperly adjusted torch or improperly positioned flame can lead to oxidation of the substrate or filler metal and result in a poor solder joint. It is also possible to introduce carbon into the substrate and filler metal by using the unburned gas portion of the flame. To prevent oxidation, the flame should not be removed once it has been applied to the joint area until the soldering process has been completed. The flame provides protection from oxidation, especially at the soldering temperature.

Temperature and Time

The flame or furnace chamber should provide enough heat to the substrate metal to reach the flow temperature of the filler metal. Then the substrate metal will be hot enough to melt the filler metal as soon as it contacts the area to be joined.

Temperature and time control the diffusion of atoms across the filler-substrate interface. Alloying can take place by diffusion if the temperature remains constant for a sufficiently long time. An alloy formed at the interface of the substrate metal and filler metal through diffusion can have properties different from those of the filler metal and the substrate metal.



• **Figure 9-5** Joining of two different substrate metals with the filler metal (in center). **Left**, Good bonding with no alloying between the filler metal and substrate metal. **Right**, A nodular region of alloying that has occurred at the interface between the filler metal and another substrate alloy, which is not distinct in this micrograph. (Courtesy Clyde E. Ingersoll.)

Figure 9-5 shows such a soldered joint between two different substrate metals. On the left side, the filler-substrate interface is represented by a sharply defined plane. On the right side, the substrate metal appears to have alloyed with the solder at the joint surface adjacent to the nodular area (to the right of the solder boundary).

Therefore the flame should be maintained in place until the filler metal has flowed completely into the connection and a short time longer to allow the flux or oxide to separate from the fluid filler metal.

CRITICAL QUESTION

What kind of heating source and surrounding environment are needed for joining titanium components?

Laser Welding of Commercially Pure Titanium

As previously noted, CP Ti is a highly reactive metal that oxidizes readily in air. At temperatures used for soldering procedures, the thickness of the titanium oxide layer increases, and it may spontaneously debond from the parent metal surface at temperatures exceeding 850 °C. Thus the quality of the soldered joint is quite variable if a traditional torch-soldering or oven-soldering procedure is used.

Laser welding in an argon atmosphere is a method of choice for joining titanium components of dental prostheses because the coherent, high-intensity laser light can be focused on a small region and melt the substrate without extensive microstructural damage to the surrounding areas. An advantage of welding is that the joint will be composed of the same pure titanium as the substrate components, thereby preserving the excellent biocompatibility potential of CP Ti and avoiding the risk of galvanic corrosion effects within the prosthesis.

CRITICAL QUESTION

Why does the ductility of a pure metal depend on its crystal structure?

Wrought Alloys and Plastic Deformation of Metals

The term *wrought alloys* refers to solid cast alloys that have been mechanically shaped to specific configurations. The process causes alteration of the cast alloy microstructures and results in significant changes in the mechanical properties. The most notable changes are the increase of the yield strength or proportional limit with a reduction of ductility. This segment reviews the crystal structure of alloys, describes mechanisms of plastic deformation, and identifies correlations between microstructural features and mechanical properties.

Theoretical and Observed Shear Strengths of Metals

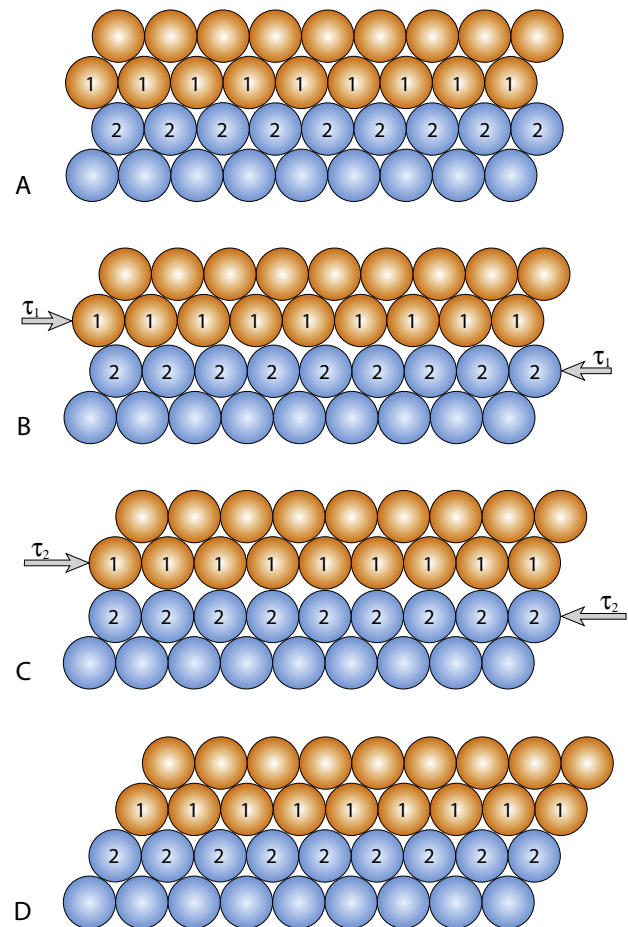
An atomic model illustrating permanent deformation of a metal having a perfect crystalline structure subjected to an applied shear stress is shown in Figure 9-6. Notice that the deformation or slip process requires the simultaneous displacement of plane 1 atoms relative to the plane 2 atoms. Studies have shown that theoretical shear strengths are much higher than those observed from mechanical testing of polycrystalline metals. For example, the differences for copper is about 35 times (7.7 GPa vs. 220 MPa), and iron is about 44 times (12.8 GPa vs. 290 MPa). The difference can be as much as 190 times greater for the ceramic SiC (31.8 GPa vs. 170 MPa). In contrast to polycrystalline materials, monocrystalline whisker specimens, which are short fibrous single crystals of metals or ceramics that achieve near perfect atomic lattice, exhibit shear strengths approaching their theoretical values. The key difference between whiskers and polycrystalline specimens of the same material is the presence of crystal imperfections at the atomic level in the polycrystalline material.

CRITICAL QUESTION

Why are the observed strengths of metals always lower than the theoretical strengths?

Crystal Imperfections

Recall Figure 2-16, which illustrates an ideal crystallization that leads to a polycrystalline structure. In reality, the growth is likely to be random and imperfect. When lattice positions have missing atoms, displaced atoms, or extra atoms, these sites are called *point defects*. The edge of an extra plane of atoms in the crystal is called

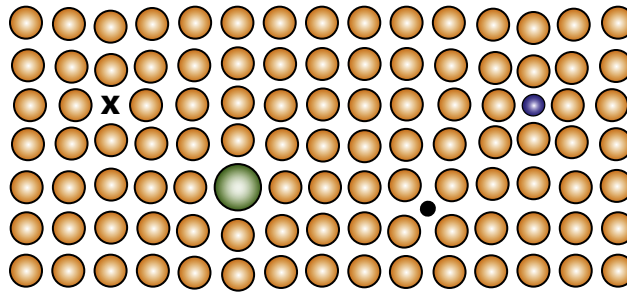


• **Figure 9-6** Slip between adjacent planes of atoms. **A**, The configuration of planes 1 (a atoms) and 2 (b atoms) when the solid is not stressed. **B**, Application of a shear stress τ_1 causes plane 1 to move with respect to plane 2. **C**, Increasing the shear stress to τ_2 increases the relative lateral displacement of the two planes. This configuration corresponds to the state of maximum stored elastic energy. **D**, The two planes have now been displaced by one interatomic distance with respect to each other. This configuration will be maintained if the load is removed. If the shear stress (τ_2) remains, the planes will continue to slip past each other.

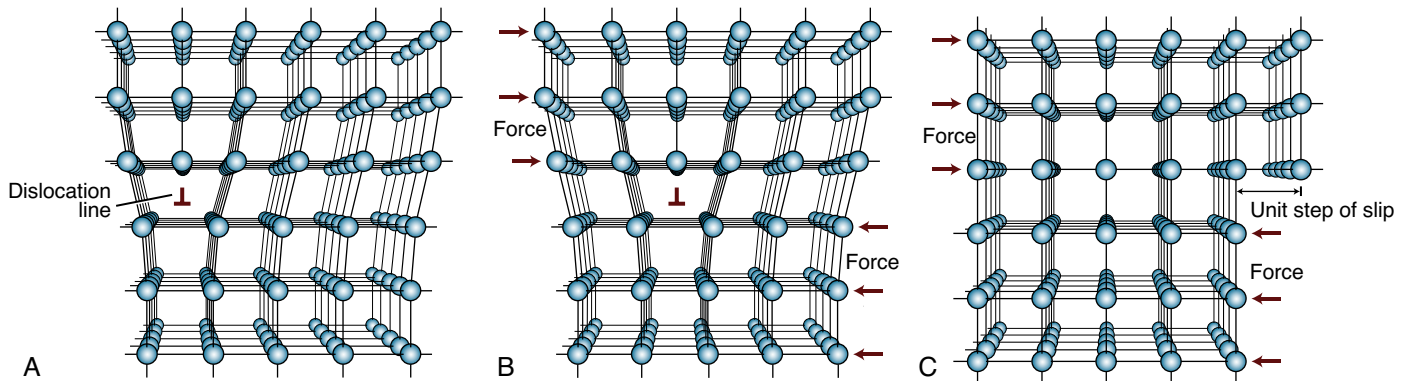
a *line defect*. The grain boundaries on the external surface of the crystal are considered two-dimensional (2-D) imperfections in the crystal.

Point Defects

Point defects are very localized disruptions in the regularity of a lattice (Figure 9-7). A *vacancy* or vacant atom site in a crystalline lattice may occur at a single site in the atomic arrangement. Foreign atoms may be present on the lattice by substituting the lattice site atoms and are known as *substitutional defects* in the crystal structure of pure metal. The size of substitutional atom may be larger or smaller than that of the normal atom in the lattice. An *interstitial defect* is produced if smaller-size atoms (such as, H, B, C, N, O) is present in the interstitial site. The vacancies provide the principal mechanism for atomic diffusion in crystalline materials. The mechanical properties of metals are also sensitive to the presence of point defects because of their interactions with dislocations discussed in the following section.



• **Figure 9-7** Point defects. “x” marks vacancy where atom is missing from the lattice. The atomic lattice can be occupied by other atoms of larger radius (*green sphere*) or smaller radius (*blue sphere*) than the atoms of host lattice, both are known as substitutional defects. Small size atom (*dark solid sphere*) occupying the interstitial space is known as interstitial defect. Note that all point defects distort the surrounding lattice.

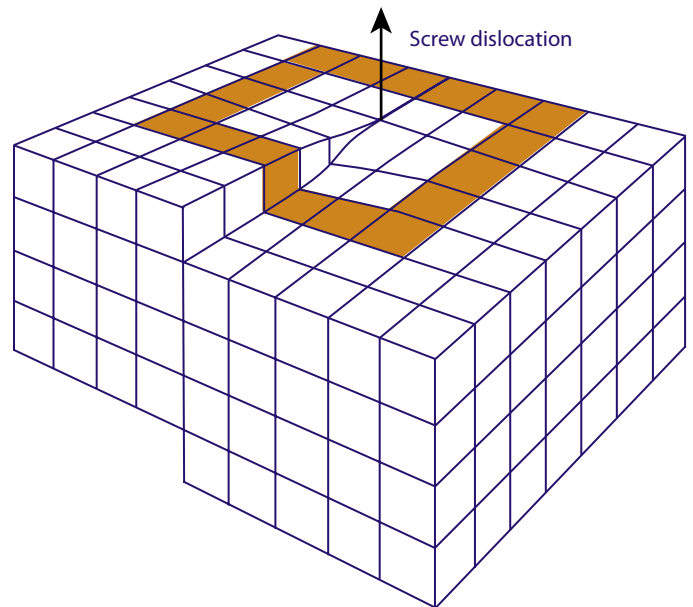


• **Figure 9-8** Illustration and movement of edge dislocation. **A**, An edge dislocation in a schematic cubic crystal structure. **B**, The dislocation has moved one interatomic distance along the slip plane under the action of the shearing force indicated by the arrows. **C**, The dislocation has reached the edge of the crystal, and a unit amount of slip has been produced. (Taken from Callister WD, Jr, Rethwisch DG: Materials science and engineering: an introduction, 8th ed, Hoboken, NJ, John Wiley & Sons, 2010.)

Line Defects (Dislocations)

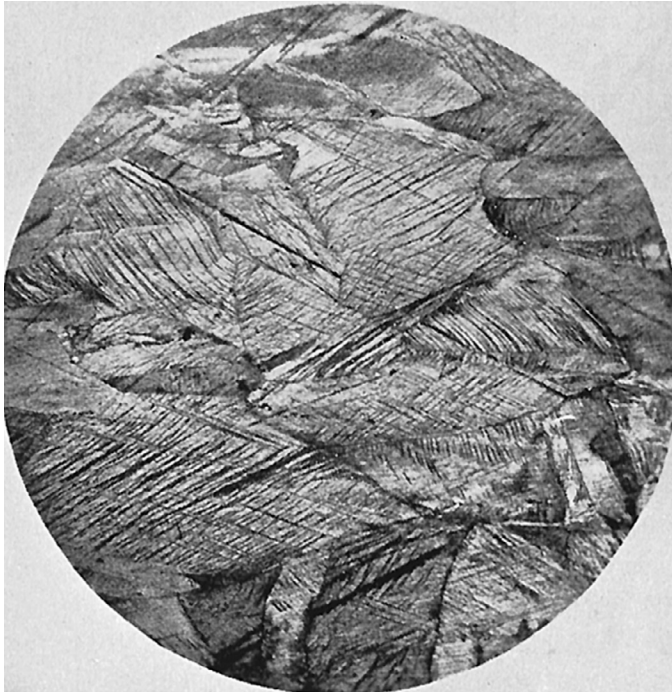
The simplest type of line defect or **dislocation**, known as an *edge dislocation*, is illustrated in **Figure 9-8, A** for a simple cubic structure. It can be noted that the atomic arrangement is regular except for the single vertical plane of atoms that is discontinuous. The edge dislocation (symbolized by \perp) is located at the edge of the partial plane. If the atoms have a helical arrangement around the dislocation line (analogous to spiral ramps in a parking garage), such arrangement is called *screw dislocation* (**Figure 9-9**).

If a sufficiently large shear stress is applied across the top and bottom faces of the crystal containing the edge dislocation shown in **Figure 9-8, A**, the bonds in the row of atoms adjacent to the dislocation will be broken, and new bonds with the next row will be established, resulting in movement of the dislocation by one interatomic distance, as indicated in **Figure 9-8, B**. Continued application of this shear stress causes similar movements of one interatomic distance until the dislocation reaches the boundary of the crystal (**Figure 9-8, C**). The plane along which an edge dislocation moves is known as a *slip plane*. The result of this dislocation movement across the crystal is that the atomic planes on one side of the slip plane have been displaced one interatomic spacing with respect to the atomic planes on the other side of the slip plane. The crystallographic direction in which the atomic planes have been



• **Figure 9-9** Illustration of screw dislocation. A crystal defect characterized by a unit distortion of part of the crystal lattice in a particular direction such that the lattice planes perpendicular to that direction form continuous helical sheets.

displaced is termed the *slip direction*, and the combination of a slip plane and a slip direction is termed a *slip system*. The screw dislocation is more difficult to visualize than the edge dislocation and is discussed in textbooks on engineering materials science. Dislocations in metallic materials often have a mixed character, consisting of both edge and screw components.



• **Figure 9-10** Photomicrograph of cold-worked gold, showing deformed grains and slip lines (the parallel lines within grains) at surface offsets where dislocations have exited their slip planes ($\times 100$). (Courtesy S. D. Tylman.)

The inherent ability of a metal to deform plastically and exhibit ductility increases with the number of slip systems associated with the crystal structure. The number of slip systems in common crystal structures is in the decreasing order of face-centered cubic (FCC; e.g., gold, silver, copper, nickel), body-centered cubic (BCC, e.g., α -iron, chromium), and then hexagonal close-packed (e.g., cobalt, zinc).

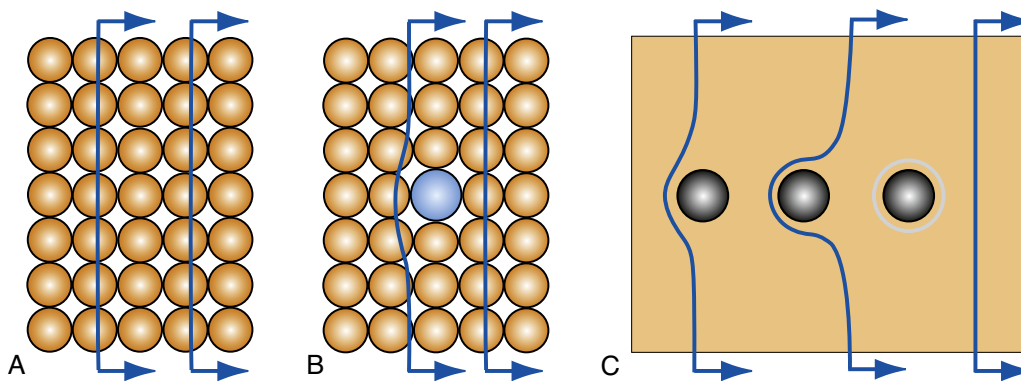
Evidently, much less shear stress is required to initiate permanent deformation of the metal crystals that contain edge dislocations (Figure 9-8) because only one row of atomic bonds along the slip plane is broken at a time, compared with the perfect crystal, where atomic bonds across the entire slip plane (Figure 9-6) must be simultaneously broken for shear deformation to occur. The proportional limit for a metal generally corresponds to the onset of significant movement of dislocations. The slip lines in Figure 9-10 correspond to slip planes where large numbers of dislocations have exited the metal, causing surface offsets that scatter the light used for observation. Thus one can conclude that permanent deformation of a metal is the result of dislocation movement and slip between atomic planes.

CRITICAL QUESTION

What fundamental strengthening mechanisms are available for alloys that are not possible for pure metals?

Dislocation Movement in Polycrystalline Alloys

Figures 9-8 and 9-11, *A* illustrate one dislocation moving in a pure metal crystal; it appears that there is little hindrance of a moving dislocation along its slip plane. In reality, there are several scenarios in which dislocation movement can be impeded in pure metals and alloys. Alloys contain multiple phases, such as solid solutions and/or precipitates (Chapter 2, [Liquid-to-Solid Transformation of Cast Metals](#)), in addition to the numerous dislocations and grain



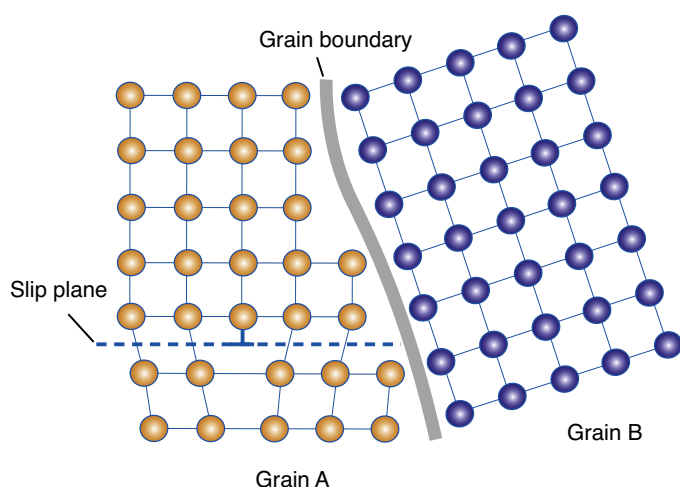
• **Figure 9-11** Effect of precipitates on the movement of edge dislocation. The illustrations depict the view taken from the top of the three-dimensional (3-D) model shown in Figure 9-8. Each line with right-pointing arrows represents a line defect (dislocation) moving toward the right side of the grain. **A**, A dislocation moves without any impediment within a grain; no extra effort is needed, and no strengthening effect occurs. **B**, The blue and slightly larger sphere represents a solute atom or coherent precipitate that presents an obstacle to the movement of the dislocation; bending of the line defect implies that the movement has been impeded, and more stress is needed to pass through the obstacle. **C**, The dark spheres represent incoherent precipitates, and the background simulates the rest of the grain. The dislocation cannot pass through the incoherent precipitate because it does not share the same lattice with the hosting grain. The first dislocation (*left*) bends as it moves close to the precipitate. The second dislocation (*middle*) continues to bend around the precipitate, while the rest of the dislocation keeps moving toward the right. Finally, the dislocation (*right*) completes its encircling around the precipitate; the rest of the dislocation rejoins and moves on through the nonstrengthened area.

boundaries found in pure metals. These crystal structural features represent obstacles that may be overcome by an application of increased stress to promote dislocation movement.

For solid-solution alloys, the atomic arrangement near solute atoms is locally distorted. The movement of dislocations along the slip plane will be impeded by the presence of such solute atoms (Figure 9-11, B). Precipitates can be coherent, where the atomic bonds are continuous across the interface with the solid-solution matrix, or incoherent, where interatomic bonds are not continuous across the interface. Coherent precipitates have the same crystal structure as the matrix phase and generate localized distortion in the atomic arrangement. Dislocations cannot move through incoherent precipitates but instead form loops of increasing size around these particles (Figure 9-11, C). Additional stress is needed to move dislocations through distorted regions, including coherent precipitates, or around incoherent precipitates.

Metals with a sufficient amount of ductility can be permanently deformed under mechanical stress at temperatures below their **recrystallization** temperatures (including room temperature), as discussed later. This process, also known as *cold working*, can create vast numbers of point defects and dislocations within the metals. These dislocations will interact with each other, mutually impeding their movements. Increased stress is required for further dislocation movement to continue the permanent deformation process.

The movement of a dislocation from one grain into another grain is unlikely, especially if the adjacent grain is misaligned (Figure 9-12). Grain boundaries represent the ends of slip planes where dislocations cease to move and accumulate. As the grain size decreases, there will be more grain boundary area per unit volume to impede dislocation motion. Grain size can be controlled by rapid cooling or quenching or by the inclusion of a grain-refining element (Chapter 2, Grain Refinement and Grain Size), such as iridium in gold alloys. Cold working also alters the shapes of grains substantially (e.g., the grains are severely elongated parallel to the wire axis).



• **Figure 9-12** This illustration shows the spatial lattices of two adjacent grains. Notice that the lattices are not aligned. There is a dislocation moving toward the grain boundary in grain A. Because of misalignment, the dislocation in grain A cannot move into grain B and is trapped at the grain boundary. In essence, the grain boundary is an obstacle to dislocation movement. Therefore the greater the number of grain boundaries, the higher is the yield strength of the material.

A higher stress, which is reflected in higher values of proportional limit, is needed for dislocations to overcome each impeding mechanism to continue moving along the slip plane. Therefore these obstacles are considered mechanisms for the strengthening of metal alloys that include solid-solution strengthening, **precipitation hardening**, **strain** (or work) **hardening**, and grain-refinement strengthening. The elastic moduli of the wrought alloys remain the same as those of their cast counterparts because there are no changes in the crystalline structure. If a phase change has occurred in the alloy in the process, some change in the elastic modulus is expected.

CRITICAL QUESTION

Why does the clasp of an RPD fracture easily after a patient has bent it back and forth repeatedly to relieve discomfort?

Effects of Strengthening Metals

The ductility of the wrought alloys is decreased with each of the strengthening mechanisms just described. The corrosion resistance of the wrought alloys is also decreased because the dislocations produce localized regions of strain at the atomic level, which have higher energy than atomic arrangements in the undeformed metal. Corrosion is a process that relieves stored energy (Chapter 3, Stress Corrosion), and it can be minimized by stress relief (discussed later).

One can observe from the first row of photomicrographs of Figure 9-13 that the thinner the specimen becomes from rolling, as designated above each photomicrograph, the flatter or thinner the grains appear to be. Although brass is used in this example, the same effect would occur with wrought dental alloys. For the extreme example of a wire, the grains will be elongated parallel to the wire axis and resemble “strands of spaghetti” in a photomicrograph showing a longitudinal section.

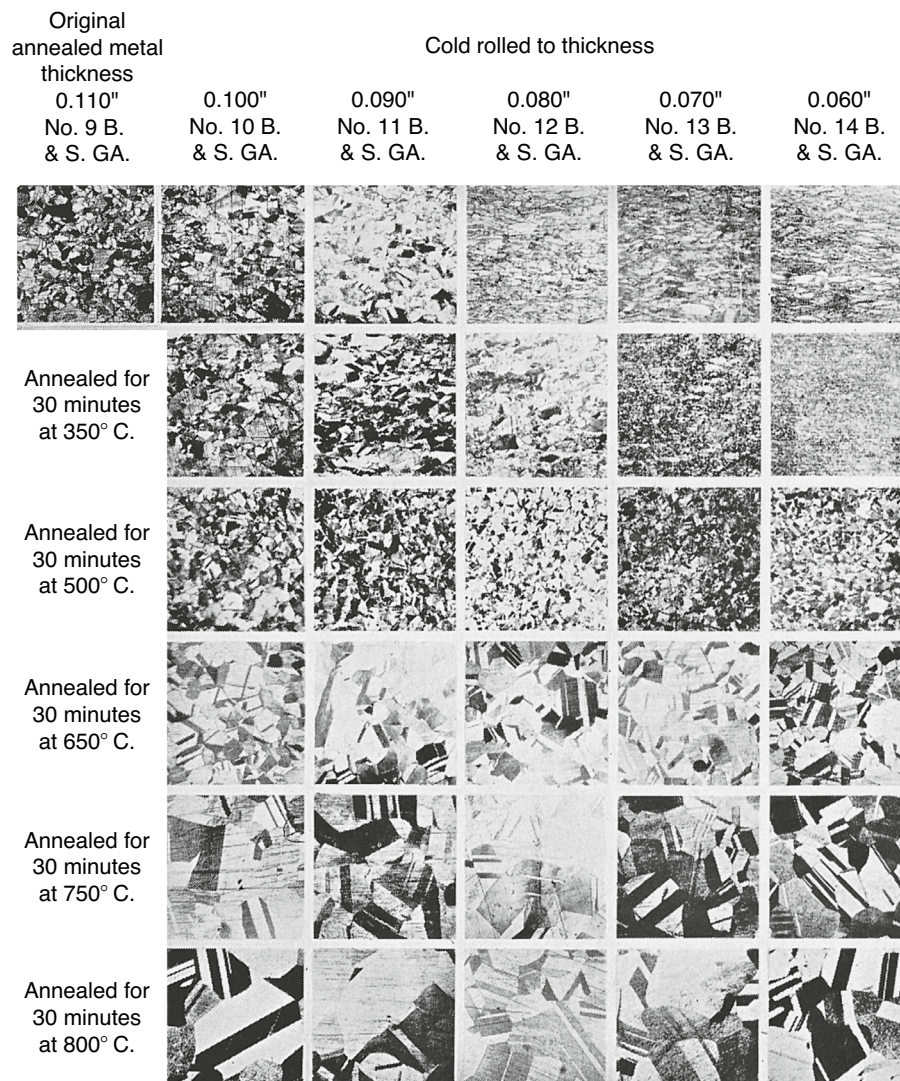
Recall the example we used in the introduction of Chapter 4 regarding the adjustment of the retentive clasps. We can conclude that the crystal deformation generates dislocations, which can be moved with finger pressure on the clasp. The movements of the dislocations allow us to shape the clasp as needed. The region near the missing half-plane of the edge dislocation can be thought of as a linear vacancy within the crystal structure. These regions accumulate when there is an edge dislocation pileup at a grain boundary and grow to a flaw of critical size. Meanwhile, greater force is needed to overcome obstacles within the alloy. Eventually, the force applied is high enough to cause crack propagation, and then fracture.

CRITICAL QUESTION

What is the difference between the twinning and dislocation-movement mechanisms of plastic deformation?

Plastic Deformation Without Dislocation Movement

An alternative mode of permanent deformation in metals is **twinning**. *Twinning* refers to the atomic arrangement within a crystal where a region takes on a special orientation from the adjacent crystal; the two different orientations are crystallographically identical, as if they are reflections across a mirror plane. This boundary between the original and the new orientation is called a *twinning plane* (Figure 9-14, A). The portion having a lattice orientation



• **Figure 9-13** Grain size and appearance of brass (copper 66%, zinc 34%) after cold working and annealing. Note that as the degree of cold working increases (*to the right in the figure*), the grains become more distorted. When the recrystallization proceeds, the grain size is inversely proportional to the degree of cold working ($\times 40$). (Prepared by L. H. DeWald.)

that is different from the original orientation is called a *twin*. Twinning can occur in a metal either during solidification, as shown in Figure 9-14, *A*, or as a result of being stressed to a state of permanent deformation (Figure 9-14, *B*).

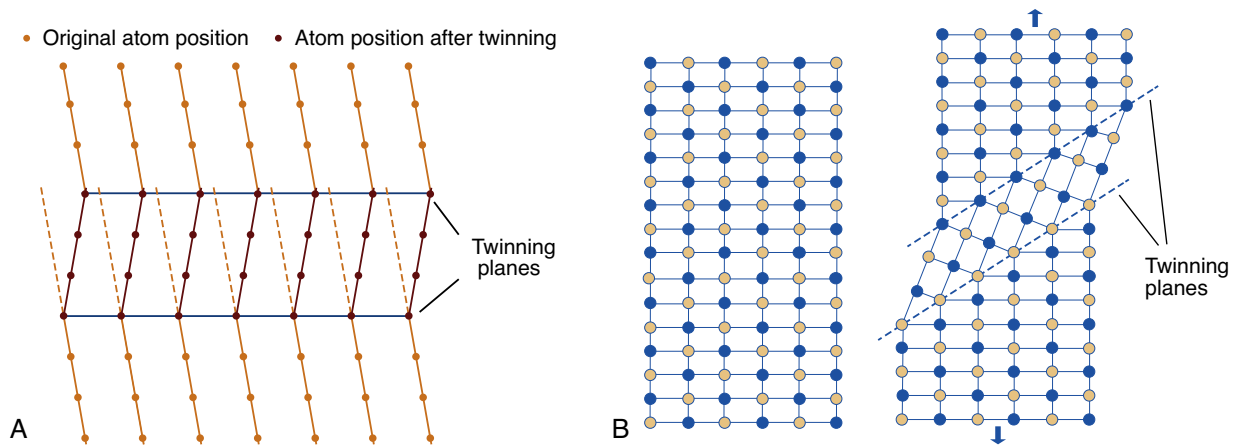
The stress needed to twin a crystal tends to be higher than that required for slip (Figure 9-6). Therefore slip is the normal permanent deformation mechanism. Twinning is the favored mechanism at high strain rates and at low temperatures, rather than dislocation movement, in metals having relatively few slip systems. One should note that permanent deformation by twinning is merely a reorientation of the lattice, and although the atoms in the twinned portion have moved, their positions relative to each other remain unchanged. On the other hand, permanent deformation by slip occurs along individual lattice planes for which the positions of atoms relative to each other have changed.

Twinning has significance for the permanent deformation of α -titanium alloys, which are highly important for some dental

implants and are gaining interest for cast restorations. In the unit cell for α -titanium, the ratio of the lattice parameter (c) in the perpendicular direction to the basal plane and the lattice parameter (a) in the basal plane (see Figure 2-9, *G*), which is known as the *cla ratio*, is slightly less than the ideal value of 1.633 for the hexagonal close-packed (HCP) structure, which results in additional slip planes and the tendency to undergo twinning readily. Twinning is also the mechanism for reversible transformation between the austenitic and martensitic structures in nickel-titanium orthodontic wires, which has considerable clinical significance.

CRITICAL QUESTION

Why must recrystallization of orthodontic wires be avoided when a stress-relief heat treatment is performed after manipulation to minimize fracture during placement?



• **Figure 9-14** Schematic illustration of twinning in a metal. **A**, Atomic arrangement at the twinning planes in a face-centered cubic metal. The dashed lines show the orientation of the crystal if twinning had not occurred. Note that the atoms on either side of the two twinning planes have a mirror relationship. **B**, A lattice structure before and after plastic deformation of a metal by twinning under tension. Note that the shape of the object has changed, but the relative position of the atoms remains unchanged. Also note that the atoms on either side of the twinning plane have a mirror relationship. The two colors of spheres provide a contrast of neighboring atoms.

Effects of Annealing Wrought Alloys

The effects associated with permanent deformation (e.g., strain hardening, decreased ductility, distorted grains, and increased dislocation density) can be reversed by simply heating the metal to an appropriate elevated temperature without melting it. This process is called **annealing**, and it takes place in three successive stages: **recovery**, **recrystallization**, and **grain growth**. The more severe the degree of cold working, the more rapidly the effects can be reversed by annealing. Also, the higher the melting point of the metal, the higher is the temperature needed for annealing.

Recovery

Heating increases atom diffusion and the initiation of annealing. As [Figure 9-15](#) shows, there is a very slight decrease in tensile strength and no change in ductility during the recovery stage, which reduces the number of dislocations and relieves the internal strain energy resulting from cold working. Orthodontic appliances fabricated by bending wires are often subjected to a stress-relief anneal prior to their placement. This heat treatment stabilizes the configuration of the appliance and allows an accurate determination of the force that the appliance can deliver in the mouth. The elimination of residual stresses in the appliance also reduces the likelihood of fracture during clinical adjustments. It is essential that this heat treatment be performed in the recovery-temperature range and not at higher temperatures where recrystallization occurs.

CRITICAL QUESTION

Why does the process of recrystallization cause a significant reduction in the tensile strength of the alloy?

Recrystallization

The recrystallization process involves a radical change in the microstructure, as seen in the second and third rows of [Figure 9-13](#). The atoms at this stage are rearranged into a lower-energy

configuration. The old, distorted grains disappear as new strain-free grains emerge. After completion of recrystallization, the alloy retains microstructures resembling that before cold working (upper-left corner of [Figure 9-13](#)) and essentially attains its original soft, ductile condition ([Figure 9-15](#)). That is the reason why recrystallization must be avoided during the stress-relief heat treatment of orthodontic appliances. If a metal is not sufficiently cold-worked, recrystallization may not occur during a typical annealing process.

The average grain size of the recrystallized structure depends on the degree of cold working; the greater is the number of such nuclei. The greater the degree of cold working, the smaller is the grain size after recrystallization.

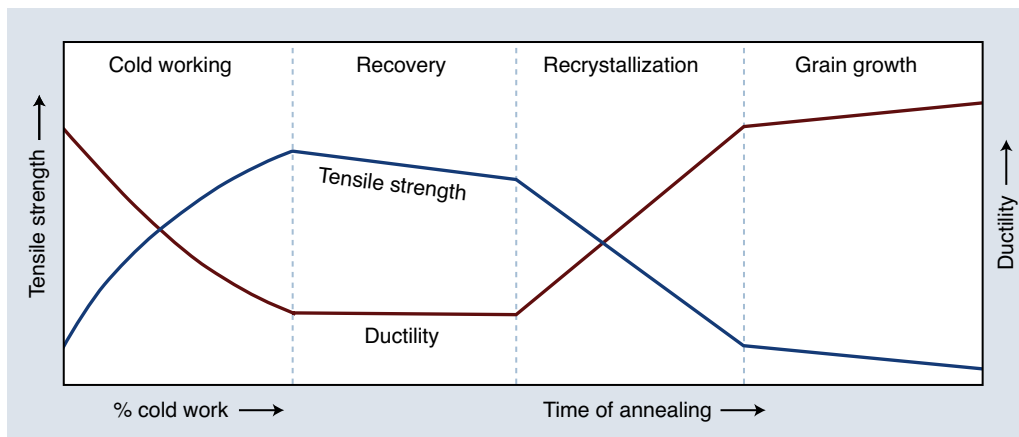
Grain Growth

The grain size increases when the cold-worked alloy is annealed at an elevated temperature ([Figure 9-13](#), row 4 to row 6). This increase in grain size is called *grain growth*, which is a process by which the volume of the grain boundary is reduced; large grains grow at the expense of small grains. Grain growth does not proceed indefinitely to yield a single crystal; rather, it ceases after a relatively coarse grain structure has been produced.

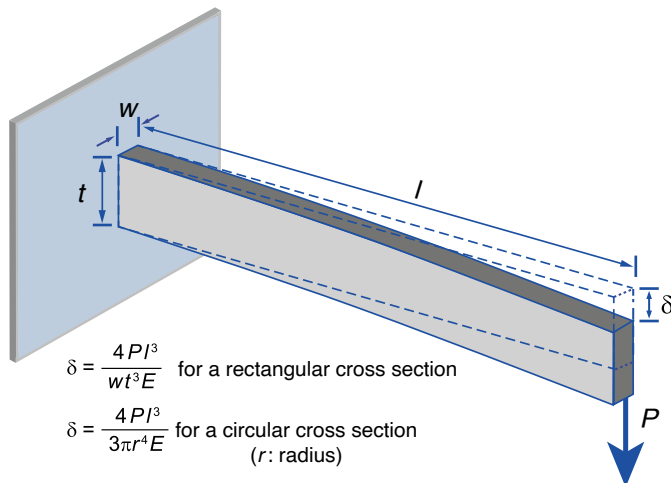
Types of Wrought Alloys

Wrought alloys are used as wires by orthodontists for correcting displacements of teeth from proper occlusion and by prosthodontists and general dentists as clasps for the retention and stabilization of RPDs. Wrought alloys are also made in the form of files and reamers for endodontists to clean and shape root canals or as prefabricated metal crowns for pedodontic patients.

Orthodontic wires are formed into various configurations or appliances to apply forces to move the teeth to a more desirable alignment. From the orthodontic viewpoint, as demonstrated by the loading of a cantilever beam ([Figure 9-16](#)), the proportional limit (or yield strength) reflects the maximal amount of force a particular beam design can deliver. The elastic deflection (δ) of



• **Figure 9-15** Tensile strength and ductility of a metal as a function of the percentage of cold working and annealing time. Tensile strength increases during cold working, and ductility decreases. These properties change only slightly during recovery. During recrystallization, tensile strength decreases, and ductility increases rapidly. Only slight changes occur during grain growth. (Adapted from Richman MH: *Introduction to the Science of Metals*, Waltham, MA, 1967, Blaisdell.)



• **Figure 9-16** Bending of a cantilever beam. δ , Deflection; t , thickness; w , width; l , length; and E , elastic modulus.

a cantilever beam under a load reflects the extent of tooth displacement that the designed appliance can deliver. The maximum elastic deflection is reached when the stress approaches the proportional limit and is called the **working range** of the beam. An obvious benefit of wrought wires is that they have a greater working range than their cast counterparts.

Physiologically, excessive forces acting on the tooth may cause root resorption, and insufficient forces yield no tooth movement. A properly designed orthodontic appliance applies appropriate amounts of force to the teeth. As the teeth move, the deflection of the device decreases. In response to the reduction in elastic deflection of the appliance, the level of force applied to the teeth is gradually reduced below the threshold level. When this happens, the appliance must be reactivated to increase the force level to its original value. Reactivation requires partial permanent deformation to obtain a suitable configuration for moving the teeth effectively.

The relationships for rectangular and round wires in Figure 9-16 show that the elastic deflection (δ) depends on the properties of

metals selected (i.e., elastic modulus and proportional limit) and the dimensions of the beam (i.e., thickness, width, radius, and length). Thus, finding the optimal design for an appliance that will deliver the low, constant forces, which are biologically desirable for tooth movement, is possible. Practically, the working range of a material is considered to be the elastic strain at the yield strength (YS) of the wire, which is termed **springback** and defined as YS/E . The mechanical principles described here also apply to the design of retentive clasps and root canal files and reamers.

Wrought alloys used in dentistry, which include stainless steel, cobalt-chromium-nickel, nickel-titanium, and beta-titanium, are now discussed.

CRITICAL QUESTION

What are the differences in the martensitic structures that form in plain carbon steels and austenitic stainless steels?

Stainless Steel Alloys

The metallurgy and terminology of stainless steels are closely related to the binary iron-carbon system, which yields the primary phases of carbon steel. Therefore a brief outline of the carbon steels is presented here.

Carbon Steel

Carbon steels can be described simply as iron-carbon binary alloys that contain less than about 2.1% of carbon by weight. At room temperature, pure iron has a bcc structure that transforms into an FCC structure at 912 °C. The solubility of carbon in BCC iron reaches a maximum of 0.02%, and this material is known as *ferrite*. The solid solution of carbon in FCC iron is called *austenite*, which has a maximal solubility of about 2.1% carbon. All carbon-steel compositions have the austenite structure at elevated temperatures.

When a plain carbon steel (only iron and carbon) containing 0.8% carbon is cooled slowly in the austenitic phase to 723 °C, a solid-state eutectoid transformation occurs to yield a microstructural constituent called *pearlite*, which consists of alternating

fine-scale lamellae of ferrite and iron carbide (Fe_3C). The Fe_3C phase is much harder and more rigid than austenite or ferrite. At temperatures below 723°C , when the carbon content is less than 0.8%, the carbon-steel microstructure consists of ferrite and pearlite, whereas plain carbon steels containing more than 0.8% carbon are much harder alloys, with microstructures consisting of iron carbide and pearlite.

If austenite is cooled very rapidly (quenched), spontaneous transformation from the FCC structure to a body-centered tetragonal (BCT) structure results in a new phase called *martensite*, which is very hard, strong, and brittle. The transformation occurs by small atomic displacements and does not involve elemental diffusion. The high hardness of martensite allows the grinding of a sharp edge, which is retained in extended use. Martensite is a metastable phase that transforms to ferrite and iron carbide when it is heated to elevated temperatures. This process is called *tempering*; it reduces the hardness of the alloy but increases its toughness.

Types of Stainless Steels

When approximately 12% to 30% chromium by weight is added to carbon steel, the alloy is commonly known as *stainless steel*. The chromium in base-metal alloys forms a very thin, transparent, adherent layer of Cr_2O_3 , termed a *passivating oxide*, which prevents corrosion of the underlying alloy. If the oxide layer is ruptured by mechanical or chemical means, the passivating oxide layer eventually forms again in an oxidizing environment, such as ambient air.

Based on the previously described crystal structures formed by iron and carbon atoms, there are three major types of stainless steels:

Ferritic Stainless Steels. These alloys provide good corrosion resistance at a low cost. They cannot be hardened by heat treatment or readily work-hardened. Consequently, they have little application in dentistry.

Martensitic Stainless Steels. These alloys can be heat-treated in the same manner as plain carbon steels, which results in a high yield strength and hardness for use in surgical and cutting instruments.

Austenitic Stainless Steels. The addition of nickel stabilizes the austenite phase on cooling of the alloy. The austenitic stainless steels are the most corrosion resistant of the three major types. Austenitic stainless steel is preferred for dental applications because it has the following properties: (1) greater ductility for more cold working without fracturing, (2) greater strength from cold work, (3) greater ease of welding, (4) ability to overcome sensitization, (5) less critical grain growth, and (6) comparative ease of reshaping.

The foregoing three classifications of stainless steels, with approximate compositions, are presented in [Table 9-15](#).

CRITICAL QUESTIONS

How does austenitic stainless steel acquire its corrosion resistance? Can this protection be lost during the fabrication and normal use of a stainless-steel appliance?

Corrosion Resistance of Austenitic Stainless Steel

Stainless steel can corrode under the conditions described in [Chapter 3, Stress Corrosion](#). For example, severe strain hardening produces highly stressed regions that are anodic to less

TABLE 9-15 Compositions (Weight Percent) of Three Types of Stainless Steel* Based on Crystal Structure of Iron Atoms

Type of Stainless Steel	Chromium	Nickel	Carbon
Ferritic (BCC)	11.5–27.0	0	0.20 max.
Austenitic (FCC)	16.0–26.0	7.0–22.0	0.25 max.
Martensitic (BCT)	11.5–17.0	0–2.5	0.15–1.20

BCC, Body-centered cubic; BCT, body-centered tetragonal; FCC, face-centered cubic.
 *Silicon, phosphorus, sulfur, manganese, tantalum, and niobium may also be present in small amounts. The balance is iron.

stressed regions in the presence of saliva. Organic or inorganic deposits and any site of surface roughness on a metal may result in localized concentration cell corrosion. Therefore a stainless-steel orthodontic appliance should be polished so that it remains clean and less susceptible to tarnish or corrosion during use. When a stainless-steel wire or a stainless-steel appliance is abraded or cut with a carbon steel bur or similar steel tool, carbon steel debris from these tools becomes embedded in the stainless-steel surface, causing dissimilar metal corrosion *in vivo*. Chlorine-containing cleansers should not be used to clean removable appliances fabricated from stainless steel.

When austenitic stainless steel is heated to between approximately 400°C and 900°C , chromium carbides precipitate along the grain boundaries, causing chromium near the grain boundaries to be depleted below the concentrations necessary for corrosion protection, which also weakens the alloy. This phenomenon is called *sensitization*; the stainless steel has become susceptible to intergranular corrosion. The temperature range of sensitization is within that used by the orthodontist for soldering and welding. In addition, filler materials that are employed for brazed or soldered joints in orthodontic appliances can also form galvanic couples *in vivo*.

The manufacturer can reduce the carbon content of the stainless steel to such an extent that carbide precipitation cannot occur or can severely cold work and heat the stainless steel within the sensitization temperature range to spread the formation of chromium carbide precipitates within the bulk grains instead of only at the grain boundaries. Elements such as titanium and tantalum, which preferentially form carbides, can be added to the stainless steel to preserve the level of chromium when the metal is exposed to elevated temperatures. This process is called *stabilization*.

Mechanical Properties of Austenitic Stainless Steel

The approximate values of the mechanical properties of a representative stainless-steel orthodontic wire are listed in [Table 9-16](#). Strength and hardness may increase with a decrease in cross-sectional dimensions because of the increased cold working that is required for forming smaller wires.

It is unfortunate that a stainless-steel orthodontic wire can become fully annealed (recrystallized) after a few seconds at temperatures from 700°C to 800°C because soldering and welding of stainless-steel wires are carried out in that temperature range. The yield strength of the wire and, thus, the working range necessary for a satisfactory orthodontic appliance are greatly reduced after such annealing. However, using low-fusing solders

TABLE 9-16 Representative Mechanical Properties for Major Orthodontic Wire Types

Alloy	Elastic Modulus (GPa)	Yield Strength (GPa)	Tensile Strength (GPa)
Stainless steel	179	1.6	2.1
Co-Cr-Ni	184	1.4	1.7
Ni-Ti	41	0.43	1.5
β -Ti	72	0.93	1.3

and minimizing the soldering and welding times can minimize the softening. Any softening that occurs under such conditions can be remedied considerably by contouring and polishing of the soldered areas.

An increase in the elastic properties of a stainless-steel wire can be obtained by heating it to temperatures between 400 °C and 500 °C for 5 to 120 seconds after cold working. This *stress-relief heat treatment* promotes the recovery annealing stage, which removes the residual stresses introduced during manipulation of the wire. Thus it stabilizes the shape of the appliance. This is important clinically because such residual stresses can promote fracture when the appliance is being adjusted by the clinician.

CRITICAL QUESTION

Which failure processes in soldered and welded joints in stainless-steel orthodontic appliances might be observed clinically?

Soldering and Welding Stainless Steel

Stainless-steel components are often joined by silver solders. Although such solders corrode in use because they are anodic to stainless steel, this is not objectionable in orthodontic appliances. These appliances are temporary structures, usually not worn in the mouth for more than 6 to 30 months, and frequent inspection by the orthodontist is necessary. As discussed earlier, a fluoride-containing flux is used to dissolve the passivating surface film formed by chromium.

Technical Considerations for Soldering

The freehand soldering of stainless steel is not greatly different from that of gold soldering, described earlier. A needlelike, non-luminous, gas-air flame may be used to minimize annealing of the metal surrounding the joint. The reducing zone of the flame should be used. The soldering should be observed in a shadow, against a black background, so that the temperature can be judged by the color of the workpiece. The color should never exceed a dull red.

Prior to soldering, the parts should be tack-welded for alignment during the soldering procedure. Then flux should be applied, and the heavier-gauge part should be heated first. Flux must cover all of the areas to be soldered before heat is applied. As soon as the flux fuses, the solder alloy should be added, and heating is then continued until the solder flows around and within the joint. After the solder has flowed, the work should be immediately removed from the heat source and quenched in water. From the preceding discussion on the sensitization of austenitic stainless steels, it should be evident that the objective during

soldering is to use as little heat for as short a time as possible. Other heating techniques include the use of a hydrogen-oxygen torch, electric resistance heating, and indirect heating using a brass wire intermediary.

CRITICAL QUESTIONS

Does welding of stainless-steel wires subject them to undesired annealing? What can be done to reduce the effect of annealing?

Welding

Flat structures such as bands and brackets are usually joined by spot welding, which produces a large electrical current that is forced by the electrode to flow through a limited area (spot) on the overlapped materials that are to be welded. The interfacial resistance of the materials to the current flow produces intense localized heating and fusion of the overlapped metals. No solder is employed. Ideally, melting is confined to the junction area, and a cast-type structure is formed. The grain structure of the surrounding wrought alloy should not be affected, but stress exists at the interface of the cast and wrought structures, which would be the most likely path of joint failure should fracture occur. The strength of the welded joint decreases with an increase in the area of recrystallization of the adjacent wrought structure, and the joint strength increases with the area of the weld. The welded joint is susceptible to corrosion, primarily because of the loss of passivation caused by sensitization and the localized stress at the interface between the weld area and the surrounding wrought structure.

Cobalt-Chromium-Nickel Alloys

Cobalt-chromium-nickel alloys were originally developed for use as watch springs (Elgiloy) and first marketed for use in orthodontic appliances during the 1950s. Elgiloy has excellent resistance to tarnish and corrosion in the oral environment, and it uses the same welding and soldering procedures used for stainless-steel wires.

The manufacturer offers Elgiloy wires in four different tempers: soft, ductile, semiresilient, and resilient. The most widely used is the soft temper (Blue Elgiloy), which is easily manipulated and then heat-treated to achieve increased resilience; other tempers are also responsive to heat treatment. The resulting changes in mechanical properties are associated with precipitation reactions. Clinicians can easily perform heat treatment using an electrical resistance welding apparatus and a special paste provided by the manufacturer to indicate the optimal period of time.

Because of their nearly identical values of elastic modulus (Table 9-16), the orthodontic force delivery for Blue Elgiloy and stainless-steel orthodontic wires is essentially the same. Heat treatment of Blue Elgiloy orthodontic wires was found to increase the elastic modulus in tension from a range of 160 to 190 GPa for as-received wires to a range of 180 to 210 GPa, along with the springback (YS/E) increase from a range of 0.0045 to 0.0065 to a range of 0.0054 to 0.0074. Co-Cr-Ni wire products are also available from other manufacturers, but minimal mechanical property data have been reported in the literature.

Nickel-Titanium Alloys

A wrought nickel-titanium orthodontic wire alloy known as *Nitinol* (now *Nitinol Classic*) was introduced commercially during the 1970s. This wire alloy is noted for its much lower elastic

modulus (Table 9-16) and much wider elastic working range compared with the stainless-steel and Co-Cr-Ni wires. The alloy name *Nitinol* originally came from the two elements, nickel (Ni) and titanium (Ti), and the Naval Ordnance Laboratory (NOL) where these alloys were developed.

The nickel-titanium alloys used in dentistry are based on the equiatomic intermetallic compound NiTi, which contains 55% nickel and 45% titanium by weight. Orthodontic wire alloys contain small amounts of other elements, such as copper and chromium. The microstructure consists predominantly of NiTi, but other very small precipitates having different compositions are also observed. The austenitic NiTi phase has a complex BCC structure, and the martensitic NiTi phase has been reported to possess a distorted monoclinic, triclinic, or hexagonal structure. The names *austenitic* and *martensitic* for these different crystallographic forms of NiTi have been taken from the metallurgical terminology for carbon steel and stainless steel.

Mechanical Properties

The approximate mechanical properties of Nitinol wire are shown in Table 9-16. The placement of permanent bends by the clinician in Nitinol wires is difficult because of their high resilience. Nitinol has high ductility, and its ability to undergo substantial work hardening is evident from the considerably higher tensile strength relative to the yield strength. The very low elastic modulus of Nitinol results in very low forces delivered by the appliance compared with similarly constructed and activated appliances from stainless steel and Co-Cr-Ni alloys, and the springback or elastic range available for tooth movement is much greater for Nitinol compared with these two alloys.

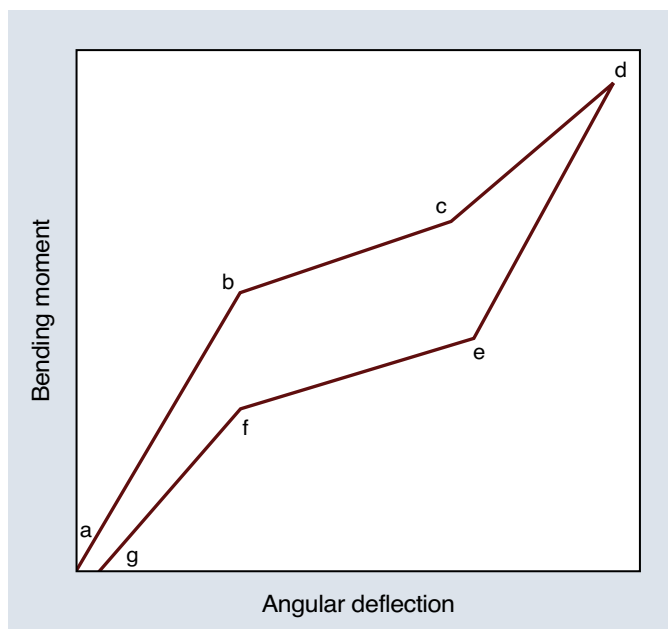
CRITICAL QUESTION

What are the clinical advantages of a shape-memory nickel-titanium orthodontic wire compared with a stainless-steel orthodontic wire?

Superelasticity and Shape Memory in Nickel-Titanium Orthodontic Wires

Transformation between the austenitic and martensitic forms of Nitinol alloys can be induced by both temperature and stress. Austenitic NiTi is the high-temperature, low-stress form, and martensitic NiTi is the low-temperature, high-stress form. Transformation between these phases occurs by a twinning process, which is reversible below the elastic limit and also results in changes in volume and electrical resistivity.

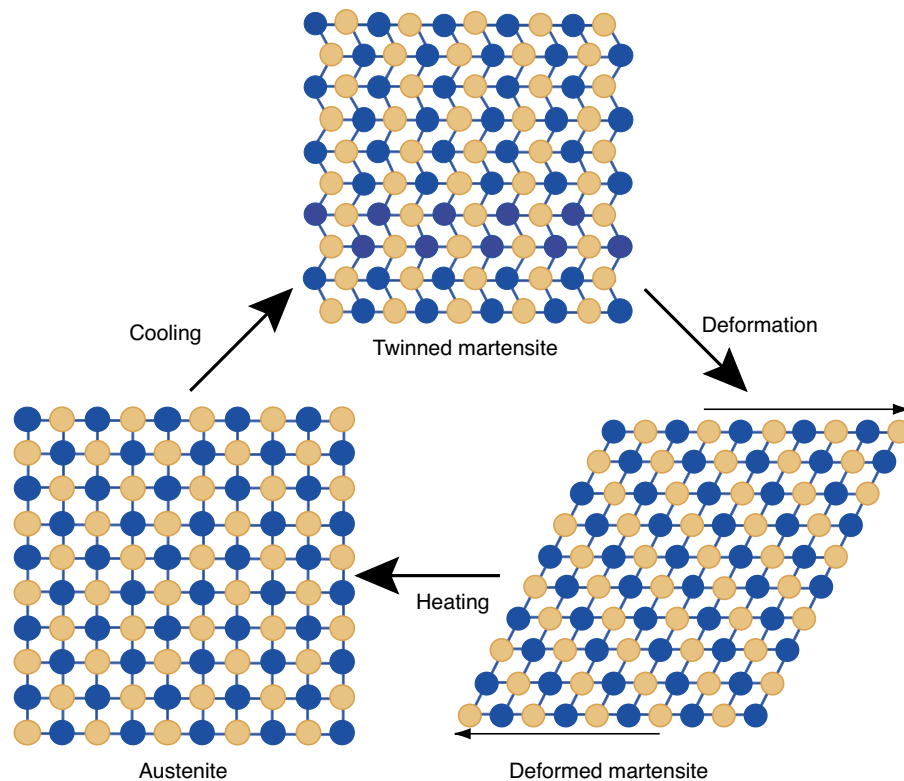
Figure 9-17 presents a highly schematic illustration of the stress-strain behavior for a certain type of NiTi wire in bending; the bending moment and the angular deflection are equivalent to the stress-versus-strain relationship tested in tension. Segment *a-b* corresponds to the initial elastic deformation of the wire, followed by segment *b-c*, where the austenitic structure transforms to the martensitic structure. After the transformation is completed at point *c* (typically at approximately 10% strain), further elastic deformation and plastic deformation occur with increasing bending moment along segment *c-d*. During unloading, this sequence of events is reversed, with segment *d-e* corresponding to loss of elastic strain (angular deflection) in the martensitic structure, followed by transformation back to the austenitic structure along segment *e-f*, and finally, loss of elastic strain in the austenitic structure along segment *f-g*, as the bending moment decreases to zero. A small amount of permanent angular deflection remains in the wire because of the permanent



• **Figure 9-17** Schematic bending movement versus angular deflection curve for a nickel-titanium orthodontic wire showing the regions of superelasticity: *b-c* during loading (activation) and *e-f* during unloading (deactivation). Such behavior imparts a large working range to the arch wire. Region *c-d* corresponds to permanent deformation during loading, and *d-e* corresponds to initial unloading of the permanently deformed arch wire. Regions *b-c* and *e-f* correspond to the forward and reverse directions, respectively, of the stress-induced transformation between the low-stress austenitic and high-stress martensitic structures. The final stage of unloading occurs along region *f-g*.

deformation induced in segment *c-d*. This behavior in segments *b-c* and *e-f* is called **superelasticity** or **pseudoelasticity** in engineering materials science. Segment *e-f* delivers a nearly constant force for tooth movement during deactivation (unloading), which does not occur with stainless-steel or Co-Cr-Ni wires. When the superelastic wire is tested in tension, for which the stress and strain are uniform over the cross section, segments *b-c* and *e-f* are both horizontal (corresponding, respectively, to the stress-assisted transformation from austenite to martensite on loading and the reverse transformation on unloading). These two regions are referred to as the *upper superelastic plateau* and the *lower superelastic plateau*, respectively. There has been some question about whether the superelastic NiTi wires are activated sufficiently into the superelastic region under clinical conditions to take advantage of this property.

Tooth movement can also be achieved by another property of some NiTi wires. The shape of the appliance, such as an orthodontic arch wire, is first established when the alloy is heated at a temperature near 480 °C to stabilize the austenitic structure (Figure 9-18). When the appliance is cooled to room temperature, the alloy converts to the twinned martensitic phase and retains its shape. The appliance is then reshaped at room temperature by the clinician; the deformed martensitic structure is altered because of the stress induced by the deformation. When it is placed into brackets bonded to malpositioned teeth, exposure of the wire to body temperature will promote the deformed martensitic structure to revert back to the austenitic structure, and the appliance regains its shape established near 480 °C, which allows for further tooth movement. This phenomenon is called **shape memory**, which



• **Figure 9-18** Shape-memory process. The austenite crystal is stable at a higher temperature and can be plastically deformed to some desired shape without altering its crystalline structure. When austenite is cooled to room temperature, it converts to a twinned martensite without undergoing a shape change. When the twinned martensite is deformed plastically under a stress, the structure detwins and takes up a new shape. Note that the overall shape of the object has changed, but the relative position between atoms did not change. Upon heating to body temperature (for orthodontic wire), the deformed martensite (detwinned martensite) will revert back to austenite and regain its original shape because there is no change in the relative position of the atom arrangement. Heating of twinned martensite will also recover the austenite structure.

is possessed at body temperature by some commercial NiTi wire products.

The temperature at which transformation from the martensitic structure to austenitic structure is completed is called the A_f (*austenite-finish*) temperature. This transformation temperature can be varied by elemental additions, such as copper and chromium, which are used for the commercial copper Ni-Ti wires to achieve different activation temperatures (27, 35, and 40 °C) in the oral environment. The A_f temperature is a clinically relevant property of an NiTi orthodontic wire, and its measurement by differential scanning calorimetry (DSC) is included in ISO Standard 15841 (ADA Specification No. 32) on wires for use in orthodontics.

These standards subdivide orthodontic wires into type 1 and type 2, which display linear elastic and nonlinear elastic behavior, respectively, during unloading from 50 °C. Stainless steel, cobalt-chromium-nickel, and β -titanium wires are type 1; nickel-titanium wires are type 2. Mechanical properties can be measured using the tension test or the three-point bending test, where the bending force during unloading is measured at 3-, 2-, 1-, and 0.5-mm deflections. Whereas type 1 wires can be tested at room temperature, type 2 wires are to be tested at 36 ± 1 °C.

As noted previously, nickel-titanium orthodontic wires are difficult to reconfigure into clinical shapes, and they must be joined by mechanical crimps because the alloy can be neither soldered

nor welded. In addition, nickel-titanium orthodontic wires have relatively rough surfaces, which result in high friction between arch wires and brackets; this can potentially prolong the time needed for clinical treatment.

CRITICAL QUESTIONS

What are the differences in the three general types of nickel-titanium orthodontic wires? Why is the superelasticity property of some NiTi alloys advantageous for endodontic applications?

Nickel-Titanium Endodontic Instruments

The outstanding property of the nickel-titanium alloy that resulted in its widespread use for endodontics is its much lower elastic modulus compared with the austenitic stainless steel that was formerly used for hand instruments. This allows the rotating NiTi file, used with an electric motor and reduction contra-angle handpiece, to negotiate curved root canals with facility. Although the pioneering article by Walia et al. investigated hand files fabricated from nonsuperelastic NiTi wire, subsequent NiTi alloys for rotary instruments were designed by manufacturers to have superelastic character with transformable austenite. The superelastic property enables the instrument to adapt along a sharply curving root canal during instrumentation, and the small increase in stress

developed at the canal wall minimizes the risk for perforation of the canal. DSC studies have shown that the enthalpy change (ΔH) for transformation between martensite to austenite in rotary NiTi instruments is less than that for superelastic orthodontic wires, indicating that transformable austenite comprises a smaller proportion of the NiTi microstructure.

The drawback of the NiTi alloy is that nickel-titanium rotary endodontic instruments have generally been fabricated by machining the starting wire blanks, in contrast to stainless-steel endodontic instruments, for which a special apparatus twists the tapered starting wire blank. However, rotary instruments have recently been introduced in which the NiTi wire blank is twisted (microstructure in the intermediate R-phase condition), rather than being machined. The machining process results in substantial permanent deformation (Figure 9-19) at the edges of the cutting flutes and surface flaws that can lead to premature fracture of the instrument. It is likely that the NiTi alloy is inherently notch sensitive because the coexisting austenitic and martensitic NiTi phases have very different crystal structures.

Recently, new NiTi alloys, beginning with M-wire, have been introduced to endodontics, for which special manufacturer thermomechanical processing yields a largely martensitic microstructure. Rotary instruments fabricated by special proprietary protocols from these new alloys have improved fatigue resistance and have become widely used in practice. The novel products from one manufacturer are described as having the property of *controlled memory*.

CRITICAL QUESTION

What is a potential clinical disadvantage of an orthodontic wire fabricated from β -titanium?

Beta-Titanium Alloys

The first commercial β -titanium orthodontic wires had an approximate composition (by weight) of 79% titanium, 11% molybdenum, 6% zirconium, and 4% tin. The addition of

molybdenum stabilizes the BCC β -titanium structure at room temperature and yields an alloy of lower elastic modulus and higher ductility than those of the HCP α -titanium alloys. This means that β -titanium can easily be drawn into wires for orthodontic applications, but careful manufacturing attention to the drawing conditions is essential. Among all β -titanium orthodontic wires available, the original commercial alloy had the trade name of *titanium-molybdenum alloy* (TMA). This orthodontic alloy composition is very close to that of the engineering Beta III titanium alloy.

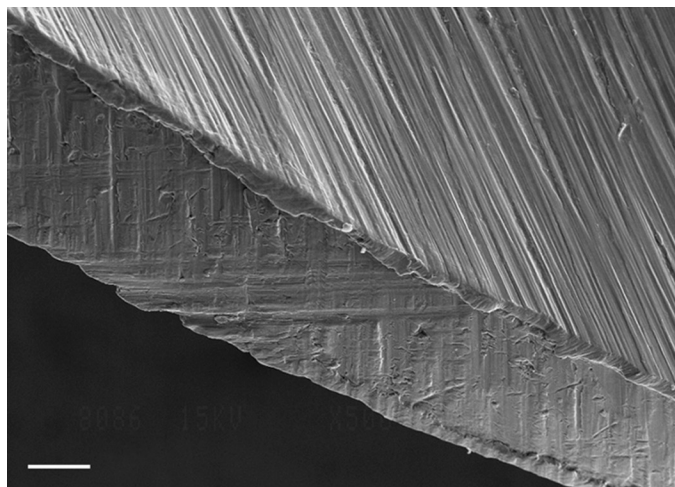
Mechanical Properties of Beta-Titanium Wires

The elastic modulus of β -titanium wires is intermediate between that for stainless-steel and Elgiloy wires and that for Nitinol wires (Table 9-16). The springback (YS/E) for β -titanium wires is much greater than that for the stainless-steel and Elgiloy wires and very similar to that for the Nitinol wires. The β -titanium wires can be highly cold-worked, and because of the BCC structure of the β phase, the wires have high formability, which is comparable to that of austenitic stainless steel, and can be readily bent into various orthodontic configurations.

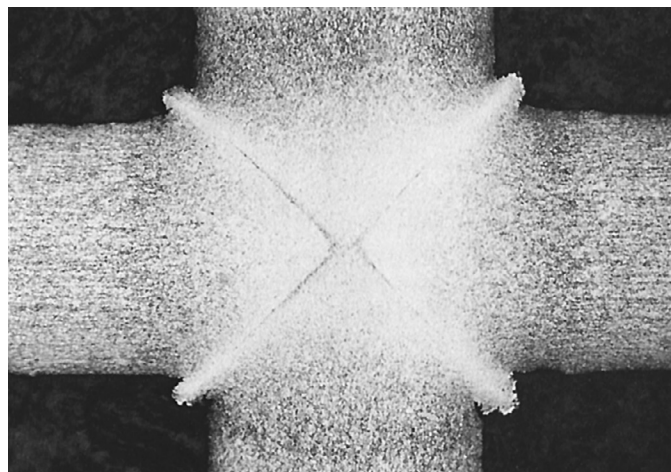
Because of the high reactivity of titanium, careful control of the original cast ingot quality, the atmosphere, and other processing parameters during wire drawing is essential. (This is also true for manufacturing of the nickel-titanium orthodontic wires.) Whereas heat treatments can be performed to alter the mechanical properties of β -titanium wires, these wires should not be heat-treated by the clinician.

Welding

Titanium alloys are highly reactive with oxygen at high temperature. Because of their high melting temperatures and this reactivity, soldering of these alloys with torches is not advisable. To prevent the potential reaction of titanium alloys with the oxygen in ambient air during the metal-joining process, these procedures are often performed in a vacuum or an argon environment. The β -titanium wires are the only orthodontic wire alloy type that demonstrates true weldability, and clinically satisfactory joints can be made by electrical resistance welding. Such joints need not



• **Figure 9-19** Photomicrograph of a nickel-titanium rotary endodontic instrument, showing permanent deformation at the edges of the flutes (roll-over) and other surface defects that resulted from the machining process used for fabrication. (Courtesy S. B. Alapati.)



• **Figure 9-20** Photomicrograph of a weld joint between two 0.43-by-0.63-mm β -titanium orthodontic wires showing minimum distortion of the original cold-worked microstructure. (Courtesy T. C. Labenski and A. J. Goldberg.)

TABLE 9-17 Physical Properties of Noble-Metal Wires

Wire Type	Yield Strength Oven-Cooled (MPa)	Tensile Strength Oven-Cooled (MPa)	ELONGATION (%)		Fusion Temperature (°C)
			Quenched	Oven-Cooled	
Formerly ANSI/ADA Type I	860	930	15	4	960
Formerly ANSI/ADA Type II	690	860	15	2	870
Wire Type	Proportional Limit (MPa)	Tensile Strength (MPa)	MINIMUM ELONGATION (%)		Fusion Temperature (°C)
			Quenched	Oven-Cooled	
Platinum-gold-palladium	550–1030*	860–1240*	14–15	—	1500–1530
Palladium-silver-copper	690–790†	960–1070†	16–24	8–15	1040–1080

ADA, American Dental Association; ANSI, American National Standards Institute.

*Quenched (alloy does not age-harden).

†Age-hardened.

Data from *Dentists Desk Reference: Materials, Instruments and Equipment. Metals and Alloys: Precious Metal Wrought Wire*, Chicago, IL, 1981, American Dental Association; Lyman T: *Metals Handbook: Properties and Selection of Metals*, ed 8, Vol 1, Metals Park, OH, 1964, American Society for Metals.

be reinforced with solder, which is necessary for welded joints in stainless-steel and Elgiloy wires. A weld made with insufficient heat will fail at the interface between the wires, whereas overheating may cause a failure adjacent to the joint. [Figure 9-20](#) is a cross section of a properly welded β -titanium joint, showing minimum distortion of the original cold-worked structure.

Corrosion Resistance

Because of a passive TiO_2 surface film, which is analogous to the Cr_2O_3 film on stainless-steel and Elgiloy wires, titanium and its alloys generally have excellent corrosion resistance and environmental stability. There has been some concern about the biocompatibility of orthodontic wires containing nickel, which may cause localized tissue irritation or an allergic reaction in some patients, and it should be noted that β -titanium is the only major orthodontic wire alloy that is nickel-free.

Surface Property

The surface roughness of the β -titanium wires is much greater than that of the stainless-steel and Elgiloy wires. Scanning electron microscopy observations suggest that the surface roughness originates from adherence of the titanium in the β -titanium alloys to the dies or rollers used in the wire-manufacturing process. Special proprietary lubricants must be used by the manufacturers to alleviate this problem. During orthodontic treatment, the rough arch-wire surfaces increase sliding friction, and localized **cold welding** of the arch-wire alloy to the metal bracket has also been hypothesized.

Surface treatment of nickel-titanium and β -titanium orthodontic wires with nitrogen ion implantation has been performed to decrease adhesion between wires and brackets. One study reported significant differences for in vitro tooth movement with ion-implanted TMA and nickel-titanium wires, compared with their non-ion-implanted counterparts. However, the results of a recent clinical study suggest that there were no significant differences for the rate of space closure when ion-implanted TMA, conventional TMA (not ion-implanted), and stainless-steel wires were used.

Additional Wrought Alloys

Noble-metal wires are still occasionally employed in the construction of RPD clasps and orthodontic appliances and in retention pins for restorations and endodontic posts. The elastic modulus of these gold alloy wires is approximately 100 to 120 GPa, which is higher than that for titanium-based wrought alloys but considerably lower than those of stainless steel and Co-Cr-Ni wrought alloys. [Table 9-17](#) shows the compositions of two types of noble-metal wrought wires and the mechanical properties of two products: platinum-gold-palladium (P-G-P), which contains 40% to 50% platinum, 25% to 30% gold, and 25% to 30% palladium by weight, and palladium-silver-copper (P-S-C), which consists of 42% to 44% palladium, 38% to 41% silver, 16% to 17% copper, and 0% to 1% platinum by weight. The high fusion temperature (hence high recrystallization temperature) of P-G-P wire would be especially useful for casting an RPD framework to this alloy. It is the high fusion temperatures of platinum and palladium that raise the fusion temperature of P-G-P wire. P-S-C wires have also been considered useful for dental applications because their fusion temperatures are higher than those of the gold-based alloy wires.

Wrought cobalt-chromium alloys for RPD clasps are also available. For example, a cobalt-chromium-tungsten-nickel wire (Ticonium) has a yield strength of approximately 920 MPa, a tensile strength of nearly 1400 MPa, and a percent elongation of 19%. This wrought alloy is not heat-treatable and is designed for use with the lower-fusing nickel-chromium-beryllium casting alloy from the same manufacturer.

Acknowledgments

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The bond strength to porcelain was not significantly different for cast Ni-Cr, cast Co-Cr, and laser-sintered Co-Cr alloys. Compositions of the Co-Cr alloys for casting and laser sintering are compared.

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Rekow D, Thompson VP: Near-surface damage—a persistent problem in crowns obtained by computer-aided design and manufacturing, *Proc Inst Mech Eng H*, 219:233–243, 2005.

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The results of this study suggest that significant differences exist in the fatigue resistance of removable denture clasps made from different commercial cast metals, which may cause loss of retention and clasp failures.

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A review article that discusses gold, platinum, and palladium colored intermetallic compounds from metal physics and crystal structure

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Bryant ST, Thompson SA, al-Omari MA, et al: Shaping ability of ProFile rotary nickel-titanium instruments with ISO sized tips in simulated root canals: Part 1 & Part 2, *Int Endod J*, 31:275–289, 1998.

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Gatto E, Matarese G, Di Bella G, et al: Load-deflection characteristics of superelastic and thermal nickel-titanium wires, *Eur J Orthod*, 35:115–123, 2013.

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Iijima M, Brantley WA, Yuasa T, et al: Joining characteristics of β -titanium wires with electrical resistance welding, *J Biomed Mater Res B*, 85:378–384, 2008.

This study shows that welding of β -titanium alloy using electrical resistance in air may not adversely affect clinically important mechanical properties. Scanning microscope observations indicated that the localized permanent deformation and the formation of an undesirable equiaxed grain structure occurred with the use of narrow electrodes.

Iijima M, Muguruma T, Brantley WA, et al: Comparisons of nanoindentation, 3-point bending, and tension tests for orthodontic wires, *Am J Orthod Dentofac*, 140:65–71, 2011.

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- Kusy RP: A review of contemporary archwires: their properties and characteristics, *Angle Orthod*, 67:197–207, 1997.
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- Miura R, Mogi M, Ohura Y, et al: The super-elastic property of the Japanese Ni-Ti alloy wire for use in orthodontics, *Am J Orthod Dentofac*, 90:1–10, 1986.
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- Sarkar NK, Redmond W, Schwaninger B, et al: The chloride corrosion behavior of four orthodontic wires, *J Oral Rehabil*, 10:121–128, 1983.
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- Shen Y, Coil JM, Zhou H, et al: HyFlex nickel-titanium rotary instruments after clinical use: metallurgical properties, *Int Endod J*, 46:720–729, 2013.
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- Walia H, Brantley WA, Gerstein H: An initial investigation of the bending and torsional properties of Nitinol root canal files, *J Endod*, 14:346–351, 1988.
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- Zinelis S, Annousaki O, Eliades T, et al: Metallographic structure and hardness of titanium orthodontic brackets, *J Orofac Orthop*, 264:426–433, 2003.
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10

Ceramic-Based Materials

OUTLINE

General Properties of Ceramic Materials

History of Dental Ceramics

Metal-Ceramic Systems

Ceramic-Ceramic or All-Ceramic Systems

CAD-CAM Processing of Ceramics

Methods for Strengthening Ceramic Restorations

Principles for Selection of Dental Ceramics

IdentCeram Certificates for Identification of Ceramic Products

KEY TERMS

Ceramic, CAD-CAM Ceramic that is formulated for the production of the whole or part of a ceramic prosthesis through the use of a computer-aided design, computer-aided manufacturing process.

Ceramic, castable Glass or other ceramic specially formulated to be cast into a refractory mold as a core coping or framework for a ceramic prosthesis.

Ceramic, core Opaque or semitranslucent crystalline dental ceramic material that provides sufficient strength, toughness, and stiffness to support overlying layers of veneering ceramics.

Ceramic, dental Inorganic compound with nonmetallic properties typically consisting of oxygen and one or more metallic (or semimetallic) and/or nonmetallic elements, such as aluminum, calcium, lithium, magnesium, potassium, silicon, sodium, tin, titanium, and zirconium. Ceramic frits that are provided in a powder form for veneering (layering) ceramics are typically composed of a mixture of glass and crystalline particles.

Ceramic, glaze Specially formulated ceramic powder that, when mixed with a liquid, applied to a ceramic surface, and heated to an appropriate temperature for a sufficient time, forms a smooth, glassy layer on a dental ceramic surface.

Ceramic, hot-pressed (pressable ceramic) Ceramic that can be heated to a flow temperature and forced under isostatic pressure to fill a cavity in a refractory mold.

Ceramic, stain Mixture of one or more pigmented metal oxides and a low-fusing glass that can modify the shade of the ceramic-based restoration; this mixture is dispersed in an aqueous medium, applied to the surface of porcelain or other dental ceramic, and heated to the vitrification temperature of this material for a specific time.

Glass-ceramic Ceramic consisting of at least one glass phase and at least one crystalline phase that is produced by a controlled crystallization of the glass.

Glass-infiltrated core ceramic A partially sintered core ceramic with a porous structure that is densified by the capillary inflow of a molten glass.

Green state Term referring to an as-pressed or minimally sintered condition prior to final sintering.

Metal-ceramic prosthesis A partial crown, full crown, or fixed partial denture made with a metal substructure to which porcelain is bonded for aesthetic enhancement via an intermediate metal oxide layer. The terms *porcelain fused to metal* (PFM), *porcelain bonded to metal* (PBM), *porcelain to metal* (PTM), and *ceramometal* are also used to describe these prostheses, but *metal-ceramic* (MC) is the term accepted internationally.

Porcelain A relatively dense, white ceramic material produced by sintering a mixture of feldspar, kaolin, quartz, and other substances, strictly referring to those containing kaolin.

Porcelain, feldspathic Ceramic composed of a glass matrix phase and one or more crystalline phases, such as leucite (KAlSi_2O_6), sanidine (KAlSi_3O_8), and apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$]. Most commercial dental porcelains designed for metal-ceramic restorations are partially crystallized feldspathic glasses that consist of tetragonal leucite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) crystals in a glass-phase matrix.

Sintering Process of heating closely packed particles below the melting point of the main component to densify and strengthen a structure as a result of bonding, diffusion, and flow phenomena.

Spinel or spinelle Crystalline mineral composed of mixed oxides such as $\text{MgO} \cdot \text{Al}_2\text{O}_3$.

Thermal compatibility Condition of low transient and residual tensile stress in ceramic adjacent to a metal or ceramic core that is associated with a small difference in the coefficients of thermal contraction between the core material and the veneering ceramic.

Transformation toughening A ceramic-strengthening mechanism that occurs through transformation of crystalline structure. For example, the stress-activated tetragonal (*t*) to monoclinic (*m*) transformation in yttria-stabilized zirconia causes slight volume expansion at the crack tip that keeps the crack from propagating and raises the stress needed to keep the crack propagation to fracture the prosthesis.

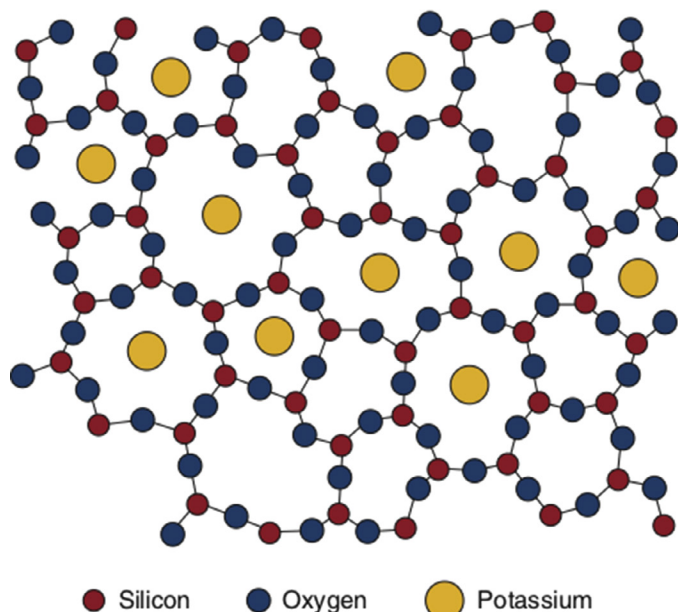
CRITICAL QUESTION

Which property best describes the fracture resistance of dental ceramics?

Dental ceramics consist of silicate glasses, **porcelains**, **glass-ceramics**, or highly crystalline solids. They are nonmetallic, inorganic structures, primarily containing compounds of oxygen with one or more metallic or semimetallic elements (aluminum, boron, calcium, cerium, lithium, magnesium, phosphorus, potassium, silicon, sodium, titanium, and zirconium). Many dental ceramics contain a crystal phase and a silicate glass matrix phase. Silicate glasses differ from nonsilicate glasses in that silicon is the central divalent cation that is bound to four relatively large oxygen anions that link in a random order to other tetrahedra to form polymeric-type $(\text{SiO}_2)_n$ chains. Their structures are characterized by chains of $(\text{SiO}_4)^{4-}$ tetrahedra in which Si^{4+} cations are positioned at the center of each tetrahedron, with O^- anions at each of the four corners (Figure 10-1). The resulting structure is not closely packed and exhibits both covalent and ionic bonds. The SiO_4 tetrahedra are linked together by sharing their corners and not their edges or faces. They are arranged as linked chains of tetrahedra, each of which contains two oxygen atoms for every silicon atom. In industry, the term *porcelain* is generally associated with ceramics produced with a significant amount of kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ or $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Kaolinite is a form of kaolin, which is a type of clay. None of the modern low-fusing or ultralow-fusing porcelains contains any clay product such as kaolinite.

General Properties of Ceramic Materials

The properties of ceramics are customized for dental applications by precisely controlling the types and amounts of the components used in their production. Ceramics exhibit chemical, mechanical, physical, and thermal properties that distinguish them from metals, acrylic resins, and resin-based composites. Most ceramics are characterized by their biocompatibility, aesthetic potential, refractory nature, high hardness, low to moderate fracture toughness,



• **Figure 10-1** Amorphous structure of potassium silicate glass.

excellent wear resistance, susceptibility to tensile fracture, and chemical inertness.

Chemical Properties

Chemical inertness is an important characteristic because this ensures that the chemically stable surface of dental restorations does not release potentially harmful elements and reduces the risk of surface roughening with increased abrasiveness or increased susceptibility to bacterial adhesion over time. The chemical inertness also makes ceramics more resistant to corrosion than plastics. Ceramics do not react readily with most liquids, gases, alkalis, and weak acids. They also remain relatively stable over long time periods, although they have been shown to undergo corrosion in simulated oral environments.

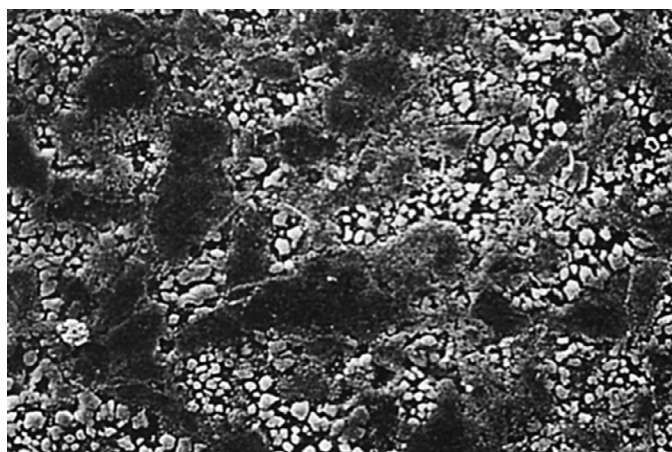
Acidulated phosphate fluoride (APF), one of the most commonly used fluoride gels for caries control, is known to etch glass by selective leaching of sodium ions, thereby disrupting the silica network. When glazed **feldspathic porcelain** is exposed to 1.23% APF or 8% stannous fluoride, surface roughness is produced within 4 minutes. As shown in Figure 10-2, a 30-minute exposure to 1.23% APF gel resulted in preferential attack of the glass phase (areas with white precipitate particles) of a body porcelain. However, the use of neutral gel, such as 0.4% stannous fluoride and 2% sodium fluoride, has no significant effect on the ceramic surface. Dentists should be aware of these long-term clinical effects of fluorides on ceramic and composite restorations and avoid the use of APF gels when composites and ceramics are present. APF gels should not be used on glazed porcelain surfaces. If the use of such a gel is needed, the surface of these restorations should be protected with petroleum jelly, cocoa butter, or wax.

CRITICAL QUESTION

If tensile strength is not a reliable property of dental ceramics, which property is a better measure of the material's fracture resistance?

Mechanical Properties

Ceramics exhibit good to excellent strength and fracture toughness. Zirconium dioxide is one of the strongest and toughest ceramics and has a flexural strength similar to that of steel, but this material's fracture toughness is much lower than that of steel. Although



• **Figure 10-2** Surface of feldspathic gingival (body) porcelain after a 30-minute exposure to 1.23% acidulated phosphate fluoride.

ceramics are strong and heat-resistant, these materials are brittle and may fracture without warning when flexed excessively or when quickly heated and cooled (i.e., under thermal shock conditions).

Resistance to Tensile Fracture

The susceptibility to tensile fracture is a drawback, particularly when flaws and tensile stress coexist in the same region of a ceramic prosthesis. Strength is not an inherent property of ceramics because this property varies with specimen size, specimen length, specimen shape, loading rate, surface preparation methods, and the environment. For example, the strength of silica-based ceramics increases with a decrease in specimen thickness, an increase in stressing rate, and a smoother surface. Such variability indicates that strength is not necessarily a bulk property because surface conditions can significantly alter the mean strength and the spread of experimental values, as indicated by the Weibull modulus and the coefficient of variation ([Chapter 4, Weibull Modulus](#)). Therefore the tensile strength of ceramics is not a useful parameter to describe the fracture resistance.

The general belief is that dental ceramics fail primarily because of their brittle nature. From a fracture mechanics point of view, the major reason for the fracture of ceramics is their low resistance to crack growth. Two fracture-mechanics properties that better explain this behavior are fracture toughness and critical strain energy release rate. Fracture toughness, which is designated as K_{Ic} , describes the critical stress intensity factor based on a Mode I (see [Figure 4-14, C](#)) crack opening under tensile stress. For dental ceramics, K_{Ic} varies from 0.8 MPa·m^{1/2} for feldspathic porcelain to 8 MPa·m^{1/2} or more for yttria-stabilized zirconia to 12 MPa·m^{1/2} or more for ceria-stabilized alumina-zirconia ceramic. In comparison, K_{Ic} values are 0.7 to 1.3 MPa·m^{1/2} for enamel, 3.1 MPa·m^{1/2} for dentin, and 0.8 to 2.5 MPa·m^{1/2} for resin composites.

The critical strain energy release rate, which is designated as G_{Ic} , is a measure of the strain energy that is released per unit increase in crack area as a ceramic with flaws or cracks is loaded progressively. The subscript *I* refers to the crack-opening mode under tension as expressed for K_{Ic} . Comparative values of K_{Ic} (MPa·m^{1/2}) versus G_{Ic} (kJ/m²) for different types of materials are as follows: (1) ductile metals, 150 versus 50 to 200; (2) brittle metals, 25 versus 1 to 5; and (3) soda-lime glass, 0.8 versus 0.5.

Abrasiveness to Enamel

In spite of their overall excellence in meeting the ideal requirements of a prosthetic material, dental ceramics can cause catastrophic wear of opposing tooth structure under certain conditions because of their hardness. Wear is a form of fracture that occurs microscopically on the surface. The most extreme damage occurs because of bruxing, premature occlusal contacts, and/or inadequate occlusal adjustments. When cuspid-guided disocclusion is ensured, the wear of opposing enamel and dentin will be greatly reduced. The abrasive wear of opposing tooth structure can be reduced further by periodically refinishing the occlusal surface after frequent exposures to carbonated beverages and/or acidulated phosphate fluoride.

The microfracture is the dominant mechanism responsible for the damage that a roughened ceramic surface can cause to tooth enamel surfaces. Enamel is susceptible to this kind of microfracture ([Figure 10-3](#)) through four specific mechanisms: (1) asperities extending from the ceramic surface that produce high localized stresses and microfracture; (2) gouging that results from high stresses and large hardness differences between two surfaces or particles extending from these surfaces; (3) impact or erosion that occurs through the action of abrasive particles carried in a



• **Figure 10-3** Excessive wear of mandibular teeth that were abraded by opposing porcelain surfaces. (Courtesy Dr. H. Young.)

flowing liquid, such as saliva; and (4) contact stress microfracture that increases localized tensile stress and also enhances the damage caused by asperities, gouging, and impact or erosion. Because of microfracture mechanisms, polishing the ceramic surface periodically to reduce the height of asperities and to minimize enamel wear rates is necessary and highly recommended.

The abrasiveness of ceramics against enamel is affected by numerous factors and properties of the crystal-phase particles and the glass matrix (if present). These include ceramic properties such as hardness, tensile strength, fracture toughness, fatigue resistance, particle-glass bonding, particle-glass interface integrity, and chemical durability. The oral environment also affects the abrasiveness, such as frequency of exposure to corrosive chemical agents (acidulated phosphate fluoride, carbonated beverages), abrasiveness of foods, residual stress, subsurface quality (voids or other imperfections), magnitude and orientation of applied forces, chewing patterns, bruxing frequency, contact area, lubrication by saliva, and duration of exposure to abrasive particles. All of these factors can lead to wear of the ceramic, with the production of roughened surfaces that can in turn abrade the opposing enamel. As a general rule, the larger the hardness difference between two sliding surfaces, the greater the degree of wear. However, this simple principle does not explain the wide variation in wear rates that is exhibited by different patients under apparently similar conditions.

CRITICAL QUESTION

How can the potential abrasive damage of tooth enamel that opposes ceramic surfaces be minimized?

Biological Properties

By virtue of their chemical inertness and resistance to corrosion, ceramics are very biocompatible restorative materials because they do not release any harmful agents to the oral environment. There have been reports of traces of lead in feldspathic-based ceramic powders up to 250 ppm. The presence of lead stems from the use of the natural mineral feldspar in the ceramic. The American Dental Association (ADA) Specification 69 states that the maximum allowable concentration of lead in dental ceramic powder is 300 ppm. The main issue is not the total amount of lead in

the powder but the leaching potential of lead or solubility of the ceramic restoration in the oral cavity. International Organization for Standardization (ISO 6872) has established a solubility testing standard for dental ceramics but no specific values for the maximum allowable release of lead. Solubility testing standards are considered harsher than the conditions in the oral environment and are representative of a lifetime of use. The amount of lead released after exposure to 4% acetic acid at 80 °C for 16 hours was not detectable according to several independent studies. The limits of detection (LOD) established for these studies were at 5 and 10 ppb (µg/L), at which no lead was detected. If lead was indeed released, the level was below the 5 ppb level and is considered insignificant.

Physical Properties

Two other important attributes of dental ceramics are their potential for matching the appearance of natural teeth and their low electrical and thermal conductivities.

Color-Matching Ability and Aesthetic Qualities

Dental ceramics are excellent in matching the appearance of natural teeth because they can display translucency, color, and chroma. Color phenomena and terminology are discussed in [Chapter 3, Color and Optical Effects](#). Perfect color matching is extremely difficult and demands exceptional skill and experience on the part of the dentist and lab technician. The structure of the tooth influences its color. Dentin is opaquer than enamel and reflects light very well. Enamel represents a predominantly crystalline layer over the dentin and is composed of tiny prisms or rods cemented together by an organic substance. The indices of refraction of the rods and the cementing substance are different. As a result, light rays are dispersed by varying proportions of absorption, transmission, scattering, and reflection to produce a resulting translucent effect and a sensation of depth as the scattered light ray reaches the eye. As light strikes the tooth surface, part of the light is reflected, and the remainder penetrates the enamel and is scattered. Any light reaching the dentin is either absorbed or partially reflected to the eye and partially scattered within the enamel. If dentin is not present, as in the tip of an incisor, some of the light rays may be transmitted into the oral cavity. As a result, this area may appear to be more translucent than that toward the gingival area. Because the law of energy conservation must apply, the following relationship shows the five energy components that are derived from the energy (E) of the incident light: $E_{\text{incident}} = E_{\text{scattered}} + E_{\text{reflected}} + E_{\text{absorbed}} + E_{\text{transmitted}} + E_{\text{fluoresced}}$.

Although some of the absorbed light may be converted into heat, some may be transmitted back to the eye as fluorescent energy. Light rays can also be dispersed, giving a color or shade that varies in different teeth. The dispersion can vary with the wavelength of the light. Therefore the appearance of the teeth may vary according to whether they are viewed in direct sunlight, reflected daylight, tungsten light, or fluorescent light. This phenomenon is called *metamerism*. The dentist and laboratory technician must reproduce the aesthetic characteristics sufficiently such that the appearance of a ceramic prosthesis is discernable only to the trained eye.

Specimens of ceramic shades are produced and distributed in a specific order in shade guides by dental ceramic manufacturers to assist dentists and lab technicians in selecting optimum ceramic shades and for communicating the desired prosthesis appearance to each other. Shade guides made of porcelain are used most often by dentists to describe the desired appearance of a natural tooth or ceramic prosthesis. However, there are several deficiencies of shade guides. Shade-guide tabs are much thicker than the thickness of

ceramic that is used for dental crowns or veneers, and they are more translucent than teeth and ceramic crowns that are backed by a nontranslucent dentin substructure, veneering ceramics that are backed by an opaque **core ceramic**, or a metal framework. Much of the incident light is transmitted through a tab. In contrast, most of the incident light on a crown is reflected except at the incisal edge and at proximal incisal areas. Furthermore, the necks of shade tabs are made from a deeper hue, and this region tends to distract the matching ability of the observer in the gingival third of the tab. To avoid this situation, some clinicians grind away the neck area of a set of shade tabs.

The production of color sensation with a pigment is a physically different phenomenon from that obtained by optical reflection, refraction, and dispersion. The color of a pigment is determined by selective absorption and selective reflection. For example, if white light is reflected from a red surface, all the light with a wavelength different from that of red is absorbed, and only the red light is reflected. If a red hue is present in a ceramic crown, but the red hue of the same wavelength is not present in the light beam, the tooth will appear as a different shade. If the tooth or restoration surface is rough, most of the light will be scattered, and little will penetrate the structure.

Conductivity

Ceramics also offer freedom from galvanic effects (low electrical conductivity). Because the metal atoms transfer their outermost electrons to the nonmetallic atoms and stabilize their highly mobile electrons, ceramics are also excellent thermal (low thermal conductivity and low thermal diffusivity) and electrical insulators. Thus tooth sensitivity associated with metallic restorations that are electrical and thermal conductors is minimized.

CRITICAL QUESTION

Which two inventions dramatically increased the success and survival probability of metal-ceramic (MC) restorations?

History of Dental Ceramics

The first porcelain tooth material was patented in 1789 by de Chemant, a French dentist, and Duchateau, a French pharmacist. This product was an improved version of “mineral paste teeth” but was not used to produce individual teeth because there was no effective way to attach the teeth to a denture base material. In 1808, Fonzi, an Italian dentist, invented a “terrometallic” porcelain tooth that was held in place by a platinum pin or frame. Plan-teau, a French dentist, introduced porcelain teeth to the United States in 1817, and Peale, an artist, developed a baking process in Philadelphia for these teeth in 1822. Commercial production of these teeth began in 1825 by Stockton. In England, Ash developed an improved version of the porcelain tooth in 1837. In 1844, the nephew of Stockton founded the S.S. White Company, which led to further refinement of the design and the mass production of porcelain denture teeth.

Dr. Charles Land, the grandfather of aviator Charles Lindbergh, introduced one of the first ceramic crowns to dentistry in 1903 using a platinum foil matrix (also known as *coping*) and high-fusing feldspathic porcelain. These crowns exhibited excellent aesthetics, but the low flexural strength of porcelain resulted in a high incidence of fractures. Although feldspathic porcelains with reliable chemical bonding have been used in MC prostheses, they were considered to be too weak to use reliably in the construction of all-ceramic crowns without a tougher ceramic core,

a cast-metal core, or metal-foil coping. Furthermore, their firing shrinkage resulted in significant discrepancies in fit and adaptation of margins unless correction firings were performed.

In 1959, Weinstein et al. filed U.S. Patent 3,052,982, which described formulations of feldspathic porcelains with a wide range of expansion coefficients that also bonded chemically to and were thermally compatible with the existing alloys of the time. The first commercial porcelain was developed by VITA Zahnfabrik around 1963. Although the first VITA porcelain products were known for their aesthetic properties, the subsequent introduction of the more versatile Ceramco porcelain (Dentsply Sirona) exhibited thermal-expansion behavior that allowed this porcelain to be used safely with a wider variety of alloys. Significant developments in the areas of MC properties, design, and performance, such as opalescence, specialized internal staining techniques, greening-resistant porcelains, porcelain butt-joint margins, and shoulder porcelains, have significantly enhanced the overall appearance and “vitality” of MC crowns and bridges and the clinical survivability of these restorations.

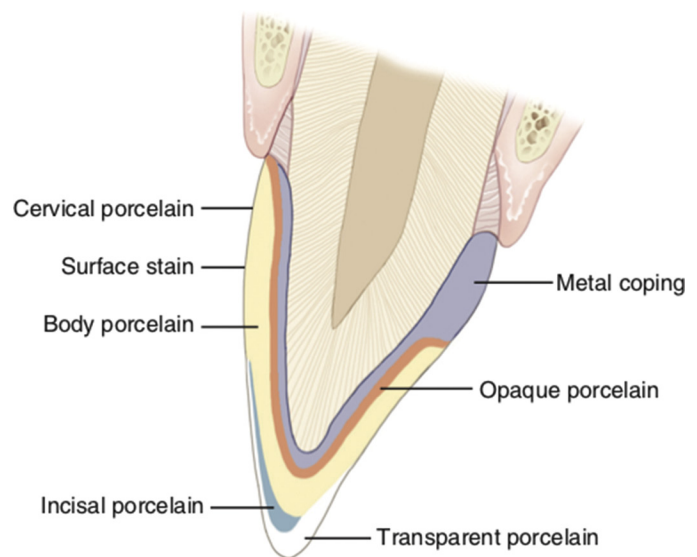
McLean and Hughes in 1965 introduced fracture-resistant all-porcelain crowns made of dental aluminous core ceramic, a glass matrix containing 40 to 50 wt% Al_2O_3 fillers. A feldspathic porcelain veneer was required to achieve acceptable aesthetics because of the chalky-white appearance of the aluminous porcelain core material. A 5-year fracture rate report showed only 2% for anterior crowns but an unacceptable 15% when aluminous porcelain was used for molar crowns. Relatively large **sintering** shrinkage (about 15% to 20%) of the core material and the use of a 20- to 25- μm -thick platinum foil have made marginal adaptation difficult to achieve except by highly skilled laboratory technicians. The principal indication for the use of aluminous porcelain crowns is the restoration of maxillary anterior crowns when aesthetics is of paramount importance.

Since the introduction of aluminous porcelain crowns and methods to produce durable MC crowns in the 1960s, improvements in the composition of ceramics and the method of forming all-ceramic crowns have greatly enhanced the ability to produce more accurate-fitting and fracture-resistant crowns made entirely of ceramic material. An all-ceramic system developed by controlling the crystallization of a glass (Dicor) was demonstrated by Adair and Grossman in 1984 and, later, a machinable glass-ceramic version (Dicor MGC), which had a tetrasilicic fluormica crystal volume of approximately 70%. In the early 1990s, a pressable glass-ceramic (IPS Empress), which contained approximately 34 vol% leucite, was introduced. A more fracture resistant, pressable glass-ceramic (IPS Empress 2) containing approximately 70 vol% of lithia disilicate crystals was introduced in the late 1990s. This core ceramic has been used for three-unit fixed dental prostheses (FDPs) as far posterior as the second premolar. Other systems based on Al_2O_3 and zirconia will be discussed later. Significant progress has been made toward the goal of developing less abrasive veneering ceramics.

In the succeeding sections, the discussion will focus on MC systems, all-ceramic systems, ceramic-strengthening mechanisms, and indications for the use of ceramic materials in greater detail.

Metal-Ceramic Systems

Several clinical studies have confirmed the high overall survival percentages of MC prostheses. In this chapter, the term *metal-ceramic* or *MC* is used synonymously with *porcelain fused to metal* (PFM), although the former term is the most internationally



• **Figure 10-4** Schematic illustration of a metal-ceramic (porcelain fused to metal) crown that has a facial metal thickness of 0.3 to 0.5 mm. It is veneered with opaque porcelain approximately 0.3 mm in thickness, and the body porcelain is about 1 mm thick.

accepted descriptor for these types of prosthetic material systems. One clinical study revealed that the fracture rate of MC crowns and bridges made from a high noble alloy was as low as 2.3% after 7.5 years. The most outstanding advantage of MC restorations is their resistance to fracture. With metal occlusal surfaces, the fracture rate in posterior sites could be reduced further. Depending on the ceramic material used, another potential advantage of MC over all-ceramic restorations is that less tooth structure needs to be removed to provide the proper bulk for the crown, especially if metal alone is used on occlusal and lingual surfaces and porcelain butt-joint margins are used on facial and buccal surfaces. Such designs also cause less wear of antagonist enamel than occurs when enamel is opposed by a ceramic surface.

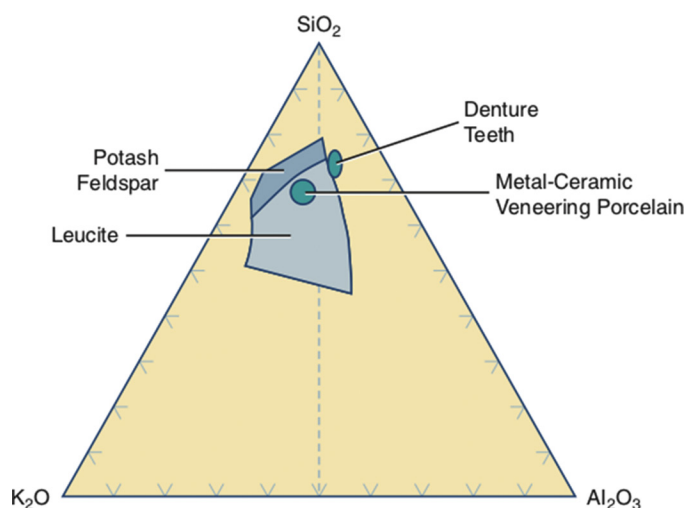
A dark line at the facial margin of an MC crown that is associated with a metal collar or metal margin is of significant concern when gingival recession occurs. This adverse aesthetic result can be minimized by designing the crown with a ceramic margin or by using a very thin knife-edge margin of metal that is veneered with opaque shoulder porcelain (Figure 10-4). This ceramic margin should be polished and/or glazed to avoid a rough surface at the margin.

One of the most frequently mentioned disadvantages is the potential for metal allergy. Such allergic reactions are very rare, except, possibly, when nickel-based alloys are used. Nonetheless, MC crowns are decreasing in popularity for use in anterior restorations. An improvement in the properties of all-ceramic crowns offers a greater potential for success in matching the appearance of the adjacent natural tooth, especially when a relatively high degree of translucency is desired. Indications may vary by patients, dentist preference, occlusion, and so forth. MC crowns are more commonly used for multiunit or posterior FDPs.

The following section focuses on the categories of ceramics, requirements of metal components, bonding of ceramic to metal, and fabrication of MC prostheses.

CRITICAL QUESTION

Which components of ceramics can cause excessive wear of tooth enamel?



• **Figure 10-5** Principal phase fields of feldspathic ceramics in the ternary K_2O - Al_2O_3 - SiO_2 system.

Ceramic Types

Conventional dental porcelain is a vitreous ceramic based on a silica (SiO_2) network and potash feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) or soda feldspar ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) or both. The ternary-phase diagram in Figure 10-5 for the K_2O - Al_2O_3 - SiO_2 system shows the approximate composition ranges of feldspathic porcelain products that are used for MC prostheses and for denture teeth. The feldspars used for dental porcelains are relatively pure and colorless. Thus pigments must be added to produce the hues of natural teeth or the color appearance of tooth-colored restorative materials that may exist in adjacent teeth. Opacifiers and glass modifiers to control the fusion temperature, sintering temperature, coefficient of thermal contraction, and solubility are also added. These ingredients are mixed together and fired to a molten state to complete the necessary chemical reaction (fusing), and then quenched in water. The resultant product, which is called *frit*, is then ground to fine powders for application.

Feldspathic Porcelains

Feldspathic porcelains contain a variety of oxides including an SiO_2 matrix (52 to 65 wt%), Al_2O_3 (11 to 20 wt%), K_2O (10 to 15 wt%), Na_2O (4 to 15 wt%), and certain additives (e.g., B_2O_3 , CeO_2 , Li_2O , TiO_2 , and Y_2O_3). These ceramics are called *porcelains* because they contain a glass matrix and one or more crystal phases, although the term *porcelain* traditionally refers to products that were produced from kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), which is a type of clay. The compositions of the veneering (layering) ceramics used for MC restorations (Table 10-1) generally correspond to those used previously for veneering aluminous porcelain core ceramic (see History of Dental Ceramics section). For MC porcelains, specific concentrations of soda, potash, and/or leucite are necessary to reduce the sintering temperature and raise the thermal expansion coefficient to a level compatible with that of the metal coping. The opaque porcelains also contain relatively large amounts of metallic oxide opacifiers to conceal the underlying metal and minimize the thickness of the opaque layer.

Feldspar has the tendency to form crystalline leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) when melted. Leucite is a potassium-aluminum-silicate mineral with a high coefficient of thermal expansion (20 to $25 \times 10^{-6}/K$) compared with that of feldspar porcelain

($8.6 \times 10^{-6}/K$). When feldspar is heated at temperatures between $1150^\circ C$ and $1530^\circ C$, this material undergoes incongruent melting to form leucite crystals in a liquid glass. Incongruent melting is the process by which one material melts to form a liquid plus a different crystalline material. The formation of leucite during melting controls the thermal expansion of the porcelain during bonding to a metal coping. Leucite has been added in feldspar porcelains to control their coefficients of thermal contraction.

Feldspathic porcelains cannot be classified as glass-ceramics because crystal formation does not occur through controlled nucleation, crystal formation, and growth. There are four types of feldspathic porcelains: (1) ultralow- and low-fusing ceramics, (2) low-fusing specialty ceramics (shoulder porcelains and wash-coat ceramics), (3) **ceramic stains**, and (4) **ceramic glazes** (autoglaze and add-on glaze).

The particle type and size of crystal fillers greatly influence the potential abrasiveness of the ceramic prosthesis. Thus the abrasiveness of the finished surface will depend on the presence or absence of crystalline fillers. When the opaque porcelain of MC restorations becomes exposed as a result of the loss of veneer, the excessive wear of enamel may occur by direct two-body contact with the opaque porcelain. When one examines the research literature investigating the potential for abrasive damage of enamel, emphasis should be placed on clinical studies that clearly describe the preparation history of the outer surface layer.

Veneering ceramics ("porcelains") for metals have higher expansion and contraction coefficients than the ceramics used to veneer alumina or zirconia core ceramics. They should not be subjected to nonessential repeated firings because this may lead to devitrification and an increased risk of cloudiness within the porcelain, in addition to potential changes in coefficient of thermal expansion (α_c) and coefficient of thermal contraction (α_c). A proper matching of these thermal properties of the alloy and porcelain is imperative to reduce the risk for chipping or cracking of the ceramic veneers, either during cooling from the sintering or glazing temperatures or at some later time in clinical service.

Ultralow-Fusing Ceramics for Metal-Ceramic Prostheses

In 1992, Duceram LFC (low-fusing ceramic; Dentsply Sirona) was marketed as an ultralow-fusing ceramic for **metal-ceramic prostheses** with three unique features: (1) this ceramic is based on a hydrothermal glass in which water is incorporated into the silicate glass structure to produce nonbridging hydroxyl groups that disrupt the glass network, thereby decreasing the glass transition temperature, viscosity, and firing temperature and increasing the coefficient of thermal expansion (CTE) to allow use as a veneer for certain low-expansion metals; (2) these types of ceramics are also claimed to be "self-healing" through a process of forming a $1\text{-}\mu\text{m}$ -thick hydrothermal layer along the ceramic surface; and (3) the extremely small size of the crystal particles (400 to 500 nm) enhances the opalescence of the ceramic by reflecting blue light hues from the surface and yellow hues from the interior of the ceramic. Other ultralow-fusing ceramics (sintering temperatures below $850^\circ C$) that are now commonly referred to as *low-fusing ceramics* have been introduced with veneering glasses that are claimed to be kinder to opposing tooth enamel, either because they are predominantly a glass phase material or because they contain very small crystal particles.

Most of the ultralow-fusing ceramics have microstructures that exhibit either a well-distributed dispersion of small crystal particles or few to no crystals. Wear studies are promising in several cases relative to the enamel wear caused by these ceramics, although not all ultralow-fusing ceramics exhibit this decreased level of abrasiveness.

TABLE 10-1 Compositions of Selected Ceramics (wt%)

Component	LOW-FUSING VACUUM PORCELAIN			METAL-CERAMIC PORCELAIN			HIP GLASS-CERAMIC	FAP GLASS-CERAMIC
	Aluminous Porcelain	Dentin	Enamel	Low-Fusing		Ultralow-Fusing	IPS e.max Press (Based on $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$)	IPS e.max Ceram Veneer Ceramic
				Dentin	Enamel			
SiO_2	35.0	66.5	64.7	59.2	63.5	60–70	57–80	45–70
Al_2O_3	53.7	13.5	13.9	18.5	18.9	5–10	0–5	5–22
CaO	1.1	2.1	1.8	—	—	1–3.0	—	1–11
Na_2O	2.8	4.2	4.8	4.8	5.0	10–15	—	4–13
K_2O	4.2	7.1	7.5	11.8	12.3	10–13	0–13	3–9
B_2O_3	3.2	6.6	7.3	4.6	0.1	0–1.0	—	—
ZnO	—	—	—	0.6	0.1	—	0–8	—
ZrO_2	—	—	—	0.4	0.1	0–1.0	0–8	—
$\text{BaO}, \text{Y}_2\text{O}_3$	—	—	—	—	—	0–0.2	—	—
SnO_2	—	—	—	—	—	0–0.2	—	—
Li_2O	—	—	—	—	—	0–1.0	11–19	—
F	—	—	—	—	—	0–1.0	—	0.1–2.5
P_2O_5	—	—	—	—	—	—	0–11	0.5–6.5
Sb_2O_3	—	—	—	—	—	0–1.0	—	—
CeO_2	—	—	—	—	—	0–0.2	—	—
TiO_2	—	—	—	—	—	1–3.0	—	—
Pigments/other	—	—	—	—	—	—	0–8/0–10	0–3
Sintering/firing temperature ($^{\circ}\text{C}$)	980	980	950	900	900	650–700	945	750

FAP, fluorapatite; HIP, hot-isostatically pressed.

Ultralow-fusing ceramics contain less Al_2O_3 and increased concentrations of CaO , K_2O , Li_2O , and Na_2O (Table 10-1).

Ultralow-fusing dentin and enamel ceramics may be easier to polish and may yield smoother and less abrasive surfaces than conventional low-fusing and medium-fusing porcelains. Because of their lower concentration of leucite crystals compared with conventional porcelains, they have lower expansion and contraction coefficients. Their lower sintering temperatures provide opportunities for use with alloys that have lower fusion temperatures, like Type 2 and 4 gold alloys, whose compositions must be modified to ensure proper chemical bonding and matched thermal expansion and contraction coefficients.

Glass Modifiers

The sintering temperature of crystalline silica is too high for use in veneering aesthetic layers onto dental casting alloys. At such temperatures, the alloys would melt. In addition, the coefficient of thermal contraction of crystalline silica is too low for these alloys. Bonds between silica tetrahedra can be broken by the addition of alkali metal ions such as sodium, potassium, and calcium. These ions are associated with the oxygen atoms at the corners of the tetrahedra and interruption of oxygen-silicon bonds. As a result, the three-dimensional (3-D) silica network contains many linear chains of silica tetrahedra that are able to move more easily at

lower temperatures than the atoms that are locked into the 3-D structure of silica tetrahedra. This ease of movement is responsible for the increased fluidity (decreased viscosity), lower softening temperature, and increased thermal expansion conferred by glass modifiers. However, too high of a modifier concentration reduces the chemical durability (resistance to attack by water, acids, and alkalis) of the glass. In addition, if too many tetrahedra are disrupted, the glass may crystallize (devitrify) during porcelain-firing operations. Hence, a balance between a suitable melting range and good chemical durability must be maintained.

Boric oxide (B_2O_3) can behave as a glass modifier to decrease viscosity, lower the softening temperature, and form a glass network. Because boric oxide forms a separate lattice interspersed with the silica lattice, this oxide still interrupts the more rigid silica network and lowers the softening point of the glass. Water, which is not an intentional addition to dental porcelain, can become a modifier. The hydronium ion, H_3O^+ , can replace sodium or other metal ions in a ceramic that contains glass modifiers. This fact accounts for the phenomenon of “slow crack growth” of ceramics that are exposed to tensile stresses and moist environments. Water also may account for the occasional long-term failure of porcelain restorations after several years of service. The role of alumina (Al_2O_3) in glass formation is complex. Alumina is not a true glass former but can take part in the glass network to alter the softening point and viscosity.

TABLE 10-2 Classification of Dental Ceramics by Sintering Temperature

Class	Applications	Sintering Temperature Range
High fusing	Denture teeth and fully sintered alumina and zirconia core ceramics	>1300 °C (>2372 °F)
Medium fusing	Denture teeth, presintered zirconia	1101–1300 °C (2013–2372 °F)
Low fusing	Crown and bridge veneer ceramic	850–1100 °C (1563–2012 °F)
Ultralow fusing	Crown and bridge veneer ceramic	<850 °C (<1562 °F)

Manufacturers employ glass modifiers to produce dental porcelains with varying firing temperatures. Dental porcelains are classified according to their firing temperatures. A typical classification is given in Table 10-2. The medium-fusing and high-fusing types are used for the production of denture teeth. The low-fusing and ultralow-fusing porcelains are used as veneering ceramics for crown and bridge construction. Some of the ultralow-fusing porcelains are used for titanium and titanium alloys because of their low-contraction coefficients that closely match those of the metals, and because the low firing temperatures reduce the risk for growth of the metal oxide. However, some of these ultralow-fusing porcelains contain enough leucite to raise their coefficients of thermal contraction as high as those of conventional low-fusing porcelains.

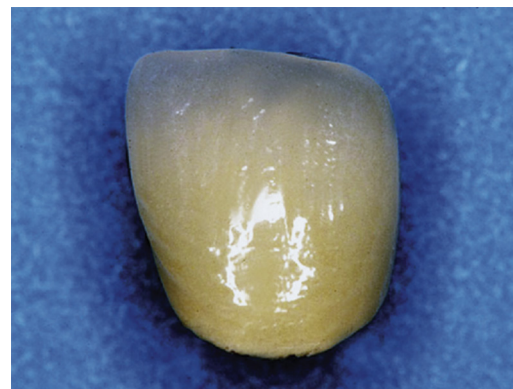
Glazes and Stain Ceramics

To ensure adequate chemical durability, a self-glaze of porcelain is preferred to an add-on glaze. A thin external layer of glassy material is formed during a firing procedure at a temperature and time that cause localized softening of the glass phase. The add-on glaze slurry material that is applied to the porcelain surface contains more glass modifiers and thus has a lower firing temperature. Keep in mind that higher proportions of glass modifier tend to reduce the resistance of the applied glazes to leaching by oral fluids.

CRITICAL QUESTION

How is the degree of sintering controlled, and what parameter defines complete sintering?

The aesthetics of porcelains for MC and ceramic prostheses, veneers, and denture teeth may be enhanced through the application of stains and glazes to provide a more lifelike appearance. Stains are simply tinted glazes that are also subject to the same chemical durability problems. However, most of the currently available glazes appear to have adequate durability if they are produced in thicknesses of 50 μm or more. To make shaded veneering ceramic to simulate stain on natural teeth, coloring pigments are first fused with feldspar, ground to fine powder, and then blended with the unpigmented powdered frit to provide the proper hue and chroma. Examples of metallic oxides and their respective color contributions to porcelain include iron or nickel oxide (brown), copper oxide (green), titanium oxide (yellowish brown), manganese oxide (laven-der), and cobalt oxide (blue). Opacity may be achieved by the addition of cerium oxide, zirconium oxide, titanium oxide, or tin oxide.



• **Figure 10-6** Autoglazed veneer ceramic.

One method for ensuring that the applied characterizing stains will be permanent is to use them internally. Internal staining and characterization can produce a lifelike result, particularly when simulated enamel craze lines and other features are built into the porcelain rather than merely applied to the surface. The disadvantage of internal staining and characterization is that the porcelain must be stripped completely if the color or characterization is unacceptable.

Autoglazed feldspathic porcelain is stronger than unglazed porcelain. The glaze is effective in sealing surface flaws and reducing stress concentrations. Figure 10-6 shows an MC crown with a properly fired autoglazed porcelain surface. If the glaze is removed by grinding, the transverse strength may be only half that of the sample with the glaze layer intact. However, the results of recent studies indicate that porcelains with highly polished surfaces have strengths comparable to those of specimens that were polished and glazed. This observation is of clinical importance. After the porcelain restoration is cemented in the mouth, the common practice for the dentist is to adjust the occlusion by grinding the surface of the porcelain with a diamond bur. This procedure weakens the porcelain, with a roughened surface that can cause increased wear of enamel. There are commercial finishing and polishing kits available for various types of ceramics (Chapter 16, Ceramic Restorations). A smoother surface also reduces the abrasion-causing damage to opposing teeth or restorations.

Glazing of feldspathic porcelain is believed to eliminate surface flaws and produce a smoother surface. However, an optimum method of producing the smoothest surface in the shortest time has not been established. Fine polishing of a roughened surface, followed by glazing will logically produce a smoother surface than polishing alone, sandblasting, followed by glazing, or diamond grinding, followed by glazing. However, even though one polishes and/or glazes a porcelain veneer surface, the surface will either slowly or markedly break down in the presence of liquids in our everyday diets, including acids such as citric acid and acetic acid. Studies have shown that these veneers will corrode over time with constant exposure to fluctuations in dietary pH changes coupled with occlusal wear.

Requirements of Metal Component

Many alloys are available to be veneered with low-fusing and ultralow-fusing porcelains. The compositions of alloys control the castability, bonding ability to porcelain, and the magnitude of stresses that develop in the porcelains during cooling from the sintering temperature. A list of typical alloy types sold by one manufacturer is presented in Table 10-3, along with the

TABLE 10-3 Composition and Properties of Typical Alloys for Metal-Ceramic (PFM) Prostheses

Alloy Product	COMPONENTS AND PROPERTIES								
	Principal Elements	Noble Metal (wt%)	ADA Class	2% Proof Stress (MPa)	Elongation (%)	Hardness (VHN)	Elastic Modulus (GPa)	CTE (25–500 °C) 10 ⁻⁶ /K	CTE (25–600 °C) 10 ⁻⁶ /K
Brite Gold	Au-Pt-In	99	HN	230	15.0	100	79	14.8	15.0
Brite GoldXH	Au-Pt	97.9	HN	355–427	11.0	180	107	14.4	14.7
Golden Ceramic	Au-Pt-Pd	97.4	HN	360	12.0	165	64	14.6	14.7
Aquarius Hard	Au-Pt-Pd	97.2	HN	455	12.0	205	88	14.5	14.8
Aquarius	Au-Pt-In	97–98	HN	320	12.0	160	79	14.6	14.8
IPS d.SIGN 98	Au-Pt	98.0	HN	510	8.0	220	80	14.3	14.6
Y	Au-Pt-Pd	96.8	HN	320	12.0	160	81	14.6	14.8
Aquarius XH	Au-Pt-Pd	96.8	HN	510	7.0	220	83	14.1	14.4
Y-2	Au-Pt-Pd	94.6	HN	380	12.0	155	83	15.0	15.1
Y-Lite	Au-Pd-Ag	93.8	HN	500	14.0	225	88	13.9	14.1
Sagittarius	Au-Pd-Pt	95.8	HN	580	10.0	245	94	14.0	14.3
Y-1	Au-Pd-Pt	87.4	HN	340	15.0	185	99	14.8	15.0
IPS d.SIGN 96	Au-Pd-Pt	87.7	HN	405	15.0	214	92	14.3	14.5
IPS d.SIGN 91	Au-Pd-In	90.6	HN	570	31.0	250	136	14.2	14.4
W	Au-Pd-Ag	80.4	HN	455	21.0	220	113	14.2	14.5
W-5	Au-Pd-Ag	78.2	HN	530	20.0	255	118	14.0	14.2
Lodestar	Au-Pd-In	90.0	HN	495	20.0	240	98	14.1	14.3
W-3	Au-Pd-In	88.3	HN	495	17.0	225	128	13.9	14.1
W-2	Au-Pd-Ag	85.3	HN	640	20.0	205	113	14.2	14.6
Evolution Lite	Au-Pd-In-Ag	89.6	HN	375	11.0	280	130	14.2	14.5
Capricorn	Pd-In-Ga-Au	84.1	N	525	21.0	260	101	14.3	14.5
IPS d.SIGN 84	Pd-In-Au-Ag	84.2	N	485	29.0	295	117	13.8	14.0
IPS d.SIGN 67	Pd-Ag-Sn-Au	66.7	N	545	15.0	240	104	13.9	14.2
Spartan Plus	Pd-Cu-Ga-Au	80.8	N	795	20.0	310	97	14.3	14.6
Capricorn 15	Pd-Ag-Au-Pd	66.9	N	490	21	255	101	14.3	14.5
Aries	Pd-Ag-Sn	63.7	N	415	46.0	185	98	14.7	14.8
IPS d.SIGN 59	Pd-Ag-Sn	59.2	N	490	14.0	230	139	14.5	14.8
IPS d.SIGN 53	Pd-Ag-Sn-In	53.8	N	545	13.0	250	132	14.8	14.9
W-1	Pd-Ag-Sn	53.3	N	485	11.0	240	114	15.2	15.4
Calisto CP+	Co-Pd-Cr-Mo	25.0	N	640	10.0	365	180	14.4	14.9
Pisces Plus	Ni-Cr-W	0	PB	600	10.0	280	183	14.1	14.4
IPS d.SIGN 15	Ni-Cr-Mo	0	PB	340	13.0	200	200	13.9	14.2
IPS d.SIGN 30	Co-Cr-Mo	0	PB	520	6.0	375	234	14.5	14.7

ADA, American Dental Association; CTE, coefficient of thermal expansion; HN, high noble; N, noble, PB, predominantly base metal; VHN, Vickers hardness number.

relevant properties of the respective alloy. The reader is referred to [Chapter 9, Requirements of Alloys for Metal-Ceramic Applications](#), for a description of other systems and the effects and purposes of the constituent metals.

The metal should have a higher melting range, with solidus temperature greater than the sintering temperature of the ceramic to prevent sag, creep (see [Figure 9-2](#)), or melting of the coping or framework during sintering and/or glazing. This deformation does not occur at oral temperatures. In addition, for gold alloys, a small amount (about 1%) of base-metal elements, such as iron, indium, and tin, is added to form a surface oxide layer during the so-called “degassing” treatment. *Degassing* is a misnomer because the primary purpose is to produce an adherent metal oxide on the surface to facilitate bonding to porcelain. Other properties of alloys of particular importance are the elastic modulus and proof strength (yield strength), which should be high enough to resist deformation, and the CTE should be closely matched to those of the ceramics. These properties, along with the oxide layer, are discussed in the following section.

CRITICAL QUESTION

What three conditions control the durability of ceramic bonding to an oxidized metal coping?

Bonding Porcelain to Metal

A durable bond between the ceramic and the metal is the primary requirement for the success of an MC restoration. When the ceramic powder is brought to sintering temperature, it melts and wets the metal surfaces. The liquid-phase ceramic then fills the surface roughness of the metal coping. Meanwhile, the liquid-glass phase reacts with metal oxide and forms an intermediate layer that adheres strongly to the ceramic and the metal coping. When the sintered MC prosthesis is cooled to room temperature, the bond between the metal and the ceramic may remain intact or become separated, depending on the extent of difference between their CTEs. These phenomena, occurring during the sintering and cooling cycle, constitute the three factors that control the durability of MC bonding: mechanical interlocking, chemical bonding, and thermal compatibility.

Recall from the discussion in [Chapters 2 \(Mechanical Interlocking\)](#) and [6 \(Mechanisms of Adhesion\)](#) that mechanical interlocking occurs when there is surface roughness. There is some evidence to support MC bonding through a mechanical interlocking mechanism. One Pd-Ag alloy was found to form metal nodules on the surface via a creep mechanism. These nodules presumably provide sufficient mechanical retention for clinical use because this alloy had been used for many years without noted problems (see [Figure 9-3](#)).

CRITICAL QUESTION

What condition is required of cast metals to achieve ionic and/or covalent bonding to veneering porcelain?

As described, metal oxides work like coupling agents in bonding ceramic to metal. The oxidation behavior of these alloys largely determines their potential for bonding with porcelain. Research into the nature of MC adherence has indicated that those alloys that form adherent oxides during the oxidation cycle also form a good bond to porcelain, whereas those alloys with poorly adherent oxides or poor bond of porcelain to the oxide ([Figure 10-7](#)) form



• **Figure 10-7** Bond failure of metal-ceramic post and core prosthesis

poor wetting. Although the thickness of the oxide is thought to play a role, there is insufficient evidence to support this theory. Rather, the quality of the oxide and this oxide's adhesion to the metal substrate appear to be the most important factors. This porcelain-metal bond is primarily ionic but is likely to have a covalent character as well and is capable of forming on smooth surfaces where little opportunity exists for mechanical interlocking.

There is a slight difference in the CTE between the metal and ceramic; usually metal has a higher value than that of the ceramic. During cooling to room temperature, the dimension of the metal coping becomes smaller relative to the ceramic, and vice versa. This means that some adjustment in the dimension at the interface must occur to keep both metal and ceramic bonded together as they cool down. The metal coping needs to be stretched somehow, and the ceramic needs to be compressed. A possible scenario is that the ceramic stretches the metal coping as the metal coping compresses the ceramic. That arrangement results in stresses developed around the interface. For example, a difference in the coefficients of thermal contraction of $1.7 \times 10^{-6}/\text{K}$ can produce a shear stress of 280 MPa in porcelain next to the MC interface when the porcelain is cooled from 954 °C to room temperature. If the shear resistance to failure is far less than 280 MPa, these stresses, resulting from thermal contraction, would likely cause spontaneous bond failure or cracking of the veneering ceramic.

The tensile stresses induced within the restoration by occlusal forces would be added to the residual thermal stresses. However, for MC systems that have an average contraction coefficient difference of $0.5 \times 10^{-6}/\text{K}$ or less (between 600 °C and room temperature), fracture is unlikely to occur except in cases of extreme stress concentration or extremely high intraoral forces. These are known as *thermally compatible systems*. Many restorations made from metal and porcelain combinations having contraction coefficient differences between 0.5 and $1.0 \times 10^{-6}/\text{K}$ are known to survive for many years. Most patients generate typical bite forces of 400 to 800 N between molar teeth and much lower forces between premolars and between anterior teeth. Thus a rather small number of patients will have bite force capabilities that are likely to cause fracture of MC crowns or bridges even when residual thermal incompatibility stresses are present. As a general rule, lower forces are generated by younger children, female patients, a more closed bite, occlusion between natural teeth, a denture, and fixed partial dentures.

The general term *compatibility* has been used in ISO 9693-1:2012 Dentistry—Compatibility Testing—Part 1: MC systems, which describe a debonding/crack-initiation strength test, to identify the ability of the MC system to demonstrate both acceptable

adhesion of ceramic to metal oxide and freedom from the crack formation associated with stresses caused by thermal expansion and contraction differences.

CRITICAL QUESTION

Why should the difference in CTEs between metal coping and respective veneering ceramic be small?

Other equally important properties of MC systems are the proportional limit (or yield strength) and elastic modulus of the metal coping. Alloys with a high modulus will also reduce the stress distribution to the ceramic from occlusion. A high proportional limit also prevents the metal coping from deforming plastically.

Various tests have been advocated for measuring the bond strength; however, the strength values obtained may not represent the true strength of the bond. Depending on the difference in CTEs of the metal and the ceramic, residual stress evolves during cooling. If a residual compressive stress evolves in the porcelain adjacent to the interfacial region, a higher bond-strength value will result, assuming that a valid test is used to produce interfacial fracture. A fracture that initiates away from the interface does not necessarily prove that the interfacial bond strength is greater than the cohesive strength of either the metal or the ceramic. This fracture may merely be caused by misalignment of loading or unintended stress distributions such that the maximum tensile or shear stresses do not occur in the interfacial region, or it may result from surface flaws that favor separation away from the interface.

For an MC bond to be maintained over time, there should be minimal residual shear stresses at the porcelain after cooling from the sintering temperature. An unfavorable stress distribution during the cooling process can result in immediate or delayed fracture of the porcelain. Thus for a successful MC restoration to be realized, both a strong interfacial bond and thermal compatibility are required.

Fabrication of Metal-Ceramic Prostheses

The fabrication of MC prostheses involves a two-step process: fabrication of the metal substructure and firing of veneering ceramic. The metal substructures are constructed using the lost wax technique, computer-aided design/computer-aided manufacturing (CAD-CAM), or 3-D printing, which is followed by finishing, polishing, and oxidation to achieve a surface oxide layer. The application of the ceramic veneer can be achieved through manual condensation or by vacuum pressing ceramic ingots.

Manual Porcelain Condensation

Ceramic for veneering MC prostheses, as well as for other applications, is supplied as a fine powder that is designed to be mixed with water or another vehicle and condensed into the desired form. The powder particles are of a particular size distribution to produce the most densely packed porcelain when properly condensed. Proper and thorough condensation is also crucial in obtaining dense packing of the powder particles. Dense packing lowers firing shrinkage and reduces porosity in the fired ceramic. This condensation may be achieved by various methods, including the vibration, spatulation, and brush techniques.

Firing Procedure

The thermochemical reactions between components of the ceramic are virtually completed during the original manufacturing process of making frits. Thus the purpose of firing is to sinter

the ceramic particles together for a specific time and temperature combination to form the prosthesis. For low-fusing porcelain, the condensed porcelain mass is placed in front of or below the muffle of a preheated furnace at approximately 650 °C. This preheating procedure permits the remaining water in the condensed ceramic mass to dissipate. Placement of the condensed mass directly into even a moderately warm furnace results in a rapid production of steam, thereby introducing voids or fracturing large sections of the veneer. After preheating for approximately 5 minutes, the porcelain is placed into the furnace, and the firing cycle is initiated.

At the initial firing temperature, the voids are occupied by the atmosphere of the furnace. As sintering of the particles begins, the porcelain particles fuse at their points of contact, and the structure shrinks and densifies. As the temperature is raised, the sintered glass gradually flows to fill up the air spaces. Air can still be trapped because the fused mass is too viscous to allow all the air to escape. An aid in the reduction of porosity in dental porcelain is vacuum firing. Sintering is complete when the structure achieves 100% of the theoretical density. However, this is unlikely to occur even in the presence of a vacuum because the possibility that all pores will be eliminated under typical dental sintering conditions is remote. A few bubbles are present, but they are markedly smaller than the ones obtained with the usual air-firing method. At a condition of 95% to 99% theoretical density, the dental veneering ceramic is said to be mature or fully sintered.

In some cases, multiple firings are necessary to fabricate a prosthesis, such as the application of a stain layer for shade adjustment or for characterization with stain lines or fine cracks. Several chemical reactions occur over time at porcelain-firing temperatures, and of particular importance are increases in the concentration of crystalline leucite. The presence of leucite content can alter the coefficient of thermal contraction of the porcelain. Some porcelains undergo an increase in leucite crystals after multiple firings that will increase their CTE. If the expansion coefficient increases above that of the metal, the expansion mismatch between the porcelain and the metal can produce stresses during cooling that are enough to cause immediate or delayed crack formation in the porcelain.

Cooling

The proper cooling of a porcelain restoration from firing temperature to room temperature is the subject of considerable importance. The catastrophic fracture of glass that has been subjected to sudden changes in temperature is a sufficiently familiar experience that most clinicians are cautious about exposing dental porcelain to rapid cooling (thermal shock) after firing. The cooling of dental porcelain, however, is a complex matter, particularly when the porcelain is bonded to a metallic substrate. Multiple firings of an MC restoration can cause the coefficient of thermal contraction of the porcelain to increase and can actually make the ceramic more likely to crack or craze because of tensile stress development.

The MC restoration that is shown schematically in Figure 10-4 has a facial metal thickness of 0.3 to 0.5 mm. This is veneered with opaque porcelain approximately 0.3 mm in thickness. The body porcelain is about 1-mm thick. Because a ductile metal is used as an inner core of an MC crown, cracks will not propagate in the metal, but they can progress through the veneering ceramic or within the interfacial region. With proper design and physical properties of the porcelain and metal, the porcelain is reinforced so that brittle fracture of the veneer can be avoided or at least minimized. Although most MC restorations involve cast metal copings, several novel noncast approaches (electrodeposition, milling, swaging, and burnishing) for the fabrication of metal

substructures have been developed in recent years. The fracture resistance of MC prostheses made from these core metals is much less reliable compared with those made from traditional cast metal copings and frameworks.

Ceramic-Ceramic or All-Ceramic Systems

Recent developments in ceramic products with improved fracture resistance, advanced CAD-CAM technology, and excellent aesthetic capability have led to a significant increase in the use of ceramic-ceramic or all-ceramic products. Ceramic crowns and bridges have been in widespread use since the beginning of the 21st century. One of the first hot-isostatically pressed (HIP) core ceramics was IPS Empress, a leucite-based glass-ceramic. Because of this material's relatively low flexure strength and fracture toughness, this glass-ceramic was limited to anterior single-unit restorations. Other ceramics that were limited to single-unit restorations were Vitadur N aluminous porcelain; Cerestore magnesia-alumina shrink-free ceramic; and Dicor, a tetrasilicic-fluormica-based glass-ceramic. Although these materials had reasonably good success rates for a few years, their limitations slowly, but surely, led to the development of stronger and tougher ceramics that allowed for a broader range of uses.

Glass-Ceramics

A glass-ceramic is a material that is formed into the desired shape as a glass, then subjected to a heat treatment to induce partial devitrification (i.e., loss of glassy structure by crystallization of the glass). The crystalline particles, needles, or plates formed during this heat-treatment process interrupt the propagation of cracks in the material when an intraoral force is applied, thereby promoting increased strength and toughness. The use of glass-ceramics in dentistry was first proposed by MacCulloch in 1968. He used a continuous glass-molding process to produce denture teeth. He also suggested that fabricating crowns and inlays by centrifugal casting of molten glass was possible.

The first commercially available **castable ceramic** material for dental use, Dicor, was developed by Corning Glass Works and marketed by Dentsply International. Dicor was a castable glass that contained 55 vol% of tetrasilicic fluormica ($\text{KMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$) and was formed into an inlay, facial veneer, or full-crown restoration by a lost wax casting process similar to that employed for metals. This product was derived from the quaternary ceramic system, K_2O - MgF_2 - MgO - SiO_2 . Besides this material's relatively low flexure strength (110 to 172 MPa) and low fracture toughness (1.6 to 2.1 $\text{MPa}\cdot\text{m}^{1/2}$), the original cast form was colorless, and prostheses needed to be colored through the application of a thin layer of shading porcelain. Subsequent products were provided as dark and light shades of machinable glass-ceramic (MGC). The flexure strength of Dicor MGC decreased by up to 88% after the tensile surface was ground.

After the glass casting core or coping was recovered from the casting investment, the glass was sandblasted to remove residual casting investment, and the sprues were gently cut away. The glass was then covered by a protective "embedment" material and subjected to a heat treatment that caused microscopic plate-like crystals of tetrasilicic fluormica to grow within the glass matrix. This crystal nucleation and crystal growth process is called *ceramming*. Once the glass was cerammed, the glass was then fit on the prepared dies, ground as necessary, and coated with veneering porcelain to match the shape and appearance of adjacent teeth. Dicor glass-ceramic was capable of producing remarkably good

aesthetics, perhaps because of the "chameleon" effect, where part of the color of the restoration was picked up from the adjacent teeth and from the tinted cements used for luting the restorations. When used for posterior crowns, the Dicor glass-ceramic crowns were more susceptible to fracture than anterior crowns.

More recently, glass-ceramics based on leucite, lithia disilicate, and hydroxyapatite have been used. These ceramics are available as powders or as solid blocks that can be machined through CAD-CAM processes or hot-pressed either as a core ceramic or as a veneering ceramic. The condensation and processing of ceramic powders are described in a previous section.

Hot-Isostatically Pressed Glass-Ceramics

Veneered leucite-based glass-ceramic core restorations are indicated for anterior veneers and crowns and premolar inlays, onlays, and crowns. Hot-pressed leucite-containing glass-ceramics have been used for many years. The technology of hot-pressing leucite-based and lithia-disilicate-based glass-ceramics is well established, and this technology has recently been applied to the hot-pressing of veneer ceramics on metals and zirconia core ceramics. The most widely used leucite-based products are IPS Empress (Ivoclar Vivadent), Cerpress SL (Leach and Dillon), Finesse (DENTSPLY Ceramco), and IPS e.max CAD (Ivoclar Vivadent). These glass-ceramics contain approximately 35 vol% of leucite ($\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$) crystals. The glass-matrix layering ceramic for these core materials also contains leucite. These glass-ceramics have relatively low flexure strength (≤ 112 MPa) and fracture toughness (1.3 $\text{MPa}\cdot\text{m}^{1/2}$), so they are not recommended for molar crowns or bridges. A partial listing of HIP core ceramics is given in [Table 10-4](#).

IPS Empress 2 (Ivoclar Vivadent), IPS Eris (Ivoclar Vivadent), and Optec OPC 3G (Pentron Laboratory Technologies) contain approximately 65 to 70 vol% of lithia disilicate ($\text{Li}_2\text{O}\cdot 2\text{SiO}_2$) as the principal crystal phase ([Table 10-1](#)). The lithia disilicate materials that are used as glass-ceramics have a narrow sintering range, which makes the processing of ceramic prostheses very technique sensitive. [Figure 10-8](#) shows a schematic cross-section of an all-ceramic crown made with a lithia disilicate core ceramic. This glass-ceramic is composed of approximately 70 vol% of lithia disilicate and 30 vol% glass. This glass base contains at least 4% ZrO_2 , which could account for this material's improved strength. This ceramic is fairly translucent but is somewhat opaquer ([Figure 10-9](#)) and a stronger core ceramic than the leucite-based glass-ceramic (Empress). The mean flexural strength of lithia disilicate is approximately 350 MPa compared with the 112 MPa strength of leucite-based glass-ceramics. This strength and a fracture toughness of 3.3 $\text{MPa}\cdot\text{m}^{1/2}$ for lithia-disilicate-based glass-ceramics are generally sufficient for most anterior and posterior crowns and for anterior three-unit bridges even though the flexural strength and fracture toughness of their layering ceramics are substantially lower. Although the core ceramic fracture resistance is moderately high, veneered prostheses have been reported to be susceptible to chipping, which may require replacement or recontouring of the affected prostheses. Examples of cracking and chipping of these prostheses are shown in [Figures 10-10](#), [10-11](#), and [10-12](#). A follow-up material to lithia disilicate is lithia silicate material, with minimal change to the physical properties. The latest iteration of these silicate glasses is the addition of lithia metasilicate to the lithia disilicate crystals with the inclusion of 10% ZrO_2 in the glass matrix.

Hot-pressed ceramics (IPS Empress, IPS Empress 2, Finesse All-Ceramic, and OPC-3G) are made by creating a wax pattern, which is invested. Similar to the lost wax technique, this

TABLE 10-4 Pressable Core Ceramics and Associated Veneering Ceramics for All-Ceramic Prostheses

Core Ceramic	Veneering Ceramic	Indications	Manufacturer
Authentic	Authentic	Veneer/inlay/onlay/anterior crown	Ceramay
Carrara Press Core	Carrara Vincent	Veneer/inlay/onlay/anterior crown	Elephant
Carrara Press Inlay	Carrara Vincent	Inlay	Elephant
Cergogold	DuceraGold	Veneer/inlay/onlay/anterior crown	Degussa
Cerpress	Sensation SL	Veneer/inlay/onlay/anterior and posterior crown	Dentagold
Cerapress	Creation LF	Veneer/inlay/onlay/anterior crown	Girrbach
Empress 2	Eris, e.max Ceram	Veneer/inlay/onlay/anterior and posterior crown/anterior FDP	Ivoclar Vivadent
e.max Press	e.max Ceram	Veneer/inlay/onlay/anterior and posterior crown/anterior FDP	Ivoclar Vivadent
Evopress	Evolution	Veneer/inlay/onlay/anterior crown	Wegold
Finesse All Ceramic	Finesse	Veneer/inlay/onlay/anterior crown	DENTSPLY Ceramco
Fortress Pressable	—	—	Mirage Dental
Magic Coating Caps Schicht-Pressing	Magic Ceram 2	Veneer/inlay/onlay/anterior crown	D.T.S. Denta TechnoStore
Magic Easy Press Colorier-Pressing	—	Veneer/inlay/onlay/anterior crown	D.T.S. Denta TechnoStore
Nuance Presskeramik	Nuance 750	Veneer/inlay/onlay/anterior crown	Schutz Dental Group
Optec OPC Low Wear	Optec OPC Low wear	Veneer/inlay/onlay/anterior and posterior crown	Jeneric Pentron
Optec OPC 3G	Optec OPC 3G Porcelain	Veneer/inlay/onlay/crown/anterior FPD	Jeneric Pentron
Trendpress	Trendkeramik LFC	Veneer/inlay/onlay/anterior crown	Binder Dental
PLATINApres	Platina M	Veneer/inlay/onlay/anterior crown	Heimerle+Meule
Vision Esthetic	Vision Esthetic	Veneer/inlay/onlay/anterior crown	Wohlwend
VITAPress	VITA Omega 900	Veneer/inlay/onlay	Vident

Adapted from Kappert HF, Krah MK: Keramiken—eine Übersicht, *Quintessenz Zahntechnik* 27(6):668–704, 2001.

investment is heated and injected under pressure into the investment mold. This technique can also be used to veneer MC prostheses, as mentioned earlier.

Fluorapatite Glass-Ceramic

Nano-fluorapatite glass-ceramic veneer, such as e.max Ceram (Table 10-1), has a relatively low CTE ($\sim 9.5 \times 10^{-6}/\text{K}$) and is matched to that of lithia disilicate glass-ceramic core material and to some alumina and zirconia ceramics. Thus, because of the higher expansion coefficients of conventional feldspathic porcelain veneers, they cannot be used on lithia disilicate core frameworks. However, the fluorapatite-based layering glass-ceramics are thermally compatible with these core glass-ceramics. Because of their sufficiently high-volume fraction of glass-matrix phase, these ceramics can be acid-etched and bonded to resin cement using well-established procedures.

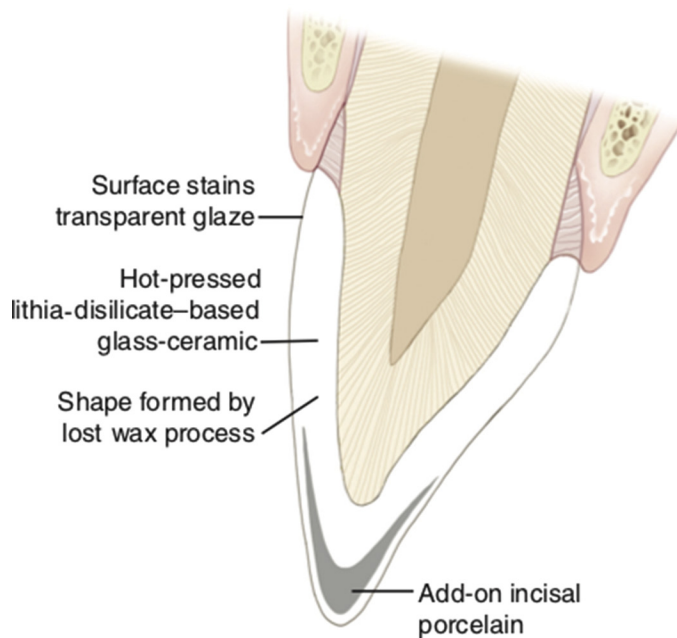
CRITICAL QUESTION

Why do zirconia-based ceramics require a stabilizer?

Zirconia-Based Ceramics

Zirconia or zirconium dioxide (ZrO_2) is a white crystalline oxide of zirconium that has an extremely low thermal conductivity, about 20% as high as that of alumina (Al_2O_3). Zirconia is chemically inert and highly corrosion resistant and exhibits unique mechanical and electrical properties that make this material extremely useful in such applications as heat insulators, oxygen sensors, and fuel cells. The first use of zirconia for medical purposes was made in 1969 in orthopedics as a new material for femoral heads on total hip replacements. Zirconia has been used in dentistry for crown and bridge applications since 2004, with the development of CAD-CAM systems. Dental zirconia should not be confused with cubic zirconia or zircon. Zircon is a naturally occurring gemstone based on zirconium silicate (ZrSiO_4), and cubic zirconia is a cubic crystalline form of zirconia. Both zircon and cubic zirconia are used as diamond simulants.

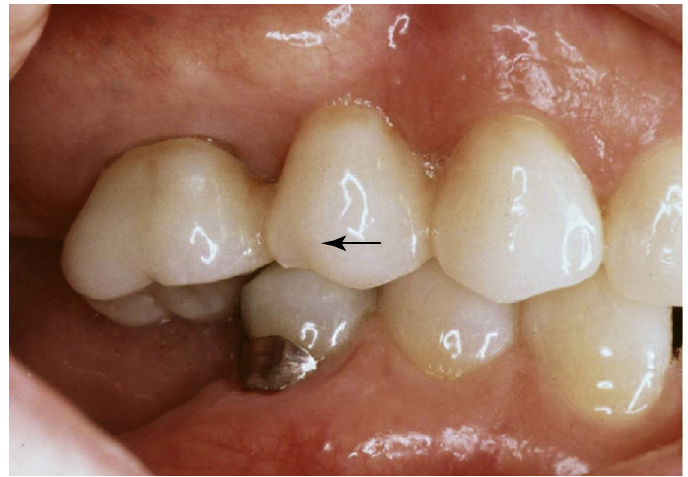
Pure ZrO_2 powder has a monoclinic crystal structure at room temperature and transforms to tetragonal between 1167 and 2367 °C, and then cubic zirconia at temperatures above 2367 °C. The transition from tetragonal to monoclinic phase results in a



• **Figure 10-8** Cross-sectional illustration of cemented Empress 2 ceramic crown with a lithia-disilicate-based ceramic core.



• **Figure 10-9** A three-unit ceramic posterior fixed dental prosthesis (tooth numbers 19-21; Fédération Dentaire Internationale tooth numbers 34 to 36) produced with a lithia-disilicate-based core ceramic.



• **Figure 10-11** Chipping of veneer ceramic on the pontic of a three-unit bridge made with a lithia-disilicate-based glass-ceramic core.

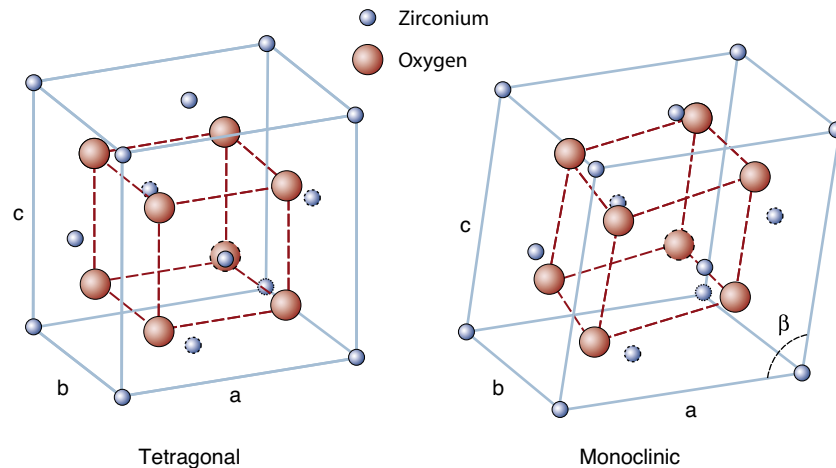


• **Figure 10-12** Chipped veneer ceramic on a pontic of a bridge made with a lithia-disilicate-based core ceramic. Also note the crack in the distal area of the posterior crown.

3% to 5% volume increase (Figure 10-13), which produces micro-cracks in bulk zirconia samples and a reduction in strength and toughness. Under this condition, pure zirconia would be useless for dental restorative applications. However, the addition of some metallic oxides to zirconia has been found to keep the tetragonal phase from transforming into the monoclinic phase as zirconia cools to room temperature, preventing the development of micro-cracks and preserving the mechanical properties of the tetragonal



• **Figure 10-10** Cracking and fracture of a crown. **A**, Crack (black arrow) in crown of a three-unit bridge made with a lithia-disilicate-based glass-ceramic core. **B**, Fracture of the crown shown.



• **Figure 10-13** Tetragonal and monoclinic unit cell structures.

phase. The process is called *doping*. The types of oxide include magnesia (MgO), lime (CaO), yttria (Y_2O_3), and ceria (Ce_2O_3). The oxide-doped zirconia is termed *stabilized zirconia*. Another possibility for stabilizing the high-temperature tetragonal phase at room temperature is to keep the crystal size to less than 10 nm during cooling.

CRITICAL QUESTION

What are the differences among fully stabilized zirconia (FSZ), partially stabilized zirconia (PSZ), and tetragonal zirconia polycrystal (TZP)?

Stabilized Zirconia

If a larger concentration of stabilizer (i.e., more than 8 mol% yttria) is added, the zirconia becomes all cubic phase and is called fully stabilized zirconia (FSZ), which is the component of cubic zirconia and devices such as oxygen sensors and fuel cells. The increase in volume does not occur in FSZ. The most common stabilizer for dental applications is yttria in the quantities of 3 to 5 mol%. At that concentration, the oxide-doped zirconia is known as partially stabilized zirconia (PSZ) or tetragonal zirconia polycrystal (TZP), depending on the microstructure. The PSZ consists of nanosized metastable tetragonal particles that have precipitated out in a cubic phase matrix approximately 50 μm in grain size during tempering of cooling cycle. Metastable tetragonal crystallites below a critical size (far below 1 μm) can be maintained in this form in a densely sintered structure down to room temperature. These crystallites allow for sintering a highly dense structure termed *TZP*, with each single crystallite that is almost 100% metastable tetragonal crystallites at room temperature. Normally, the material is designated by the quantity of stabilizer before the abbreviation of the stabilizer, and then the type of microstructure. Therefore *3Y-TZP* refers to 3 mol% Y_2O_3 tetragonal zirconia polycrystal, and *5Y-PSZ* has 5 mol% Y_2O_3 partially stabilized zirconia. Magnesia has also been used to produce an Mg-PSZ core ceramic (ZirMagnum, Cad.esthetics AB, Skellefteå, Sweden). Ceria is used as a stabilizer in a Ce-TZP/ Al_2O_3 core ceramic (KZR-CAD NANOZR, Yamakin Co. Ltd., Osaka, Japan).

High strengths were discovered to correlate with a high tetragonal phase content, whereas a high amount of monoclinic phase leads to low strengths. For example, the fracture toughness of a 92% dense nondoped monoclinic zirconia has been reported to be

2.1 $\text{MPa}\cdot\text{m}^{1/2}$, and the fracture toughness of tetragonal 3Y-TZP is approximately 8 to 10.3 $\text{MPa}\cdot\text{m}^{1/2}$. This improvement was identified to have been caused by a tetragonal-to-monoclinic transformation, which will be discussed in the following section.

CRITICAL QUESTION

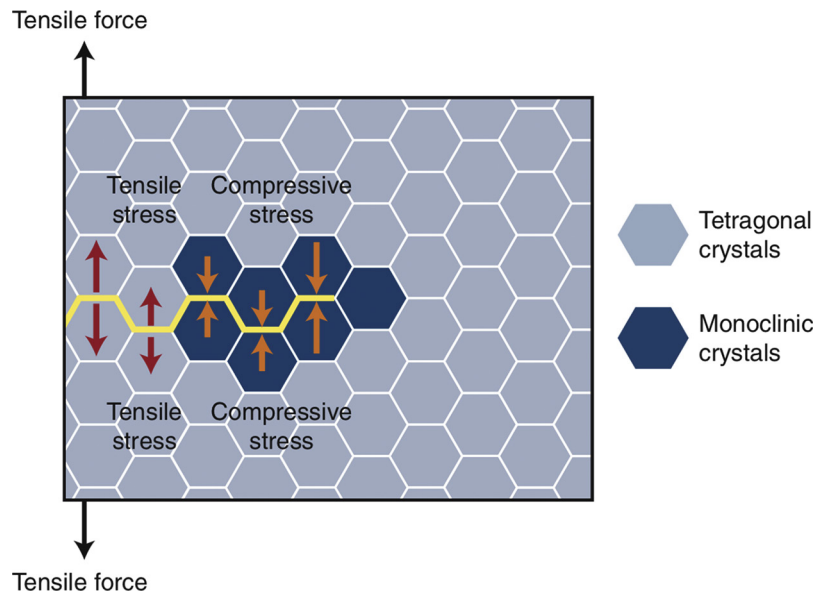
What microstructural changes occur in 3Y-TZP ceramic at the tip of cracks in the presence of tensile stress?

Through what mechanism does transformation toughening increase the resistance of yttria-stabilized zirconia to fracture?

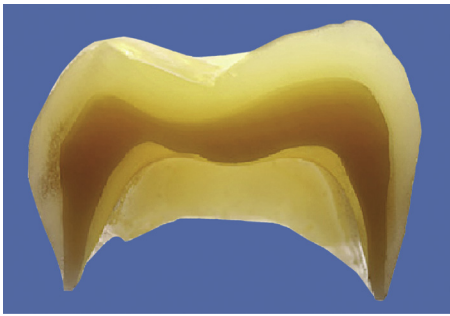
Transformation Toughening

The structural stabilization of zirconia by yttria results in a significant proportion of metastable tetragonal phase. By controlling the composition, particle size, and temperature-versus-time cycle, zirconia can be densified by sintering at a high temperature, and the tetragonal structure can be maintained as individual grains (i.e., TZP) or precipitates (i.e., PSZ), as the structure is cooled to room temperature. The tetragonal phase is retained in a metastable state at room temperature by internal stress and can transform under certain conditions to a stable monoclinic phase with a corresponding volume increase. When sufficient stress develops in the structure, and a crack begins to propagate, causing the metastable tetragonal crystals (grains) or precipitates next to the crack tip to release the internal stress, the metastable tetragonal phases transform to the stable monoclinic form. In this process, a 3 vol% expansion of the ZrO_2 crystals or precipitates occurs that places the crack under a state of compressive stress (Figure 10-14), and crack progression is arrested. To advance this crack further, additional tensile stress would be required. This phenomenon increases the flexural and tensile fracture resistance of stabilized zirconia prostheses and, presumably, the survival probabilities of zirconia-based restorations and is therefore called **transformation toughening**. Because of this strengthening and toughening mechanism, the yttria-stabilized zirconia ceramic is sometimes referred to as *ceramic steel*. Figure 10-15 shows a cross-sectional view of a Lava crown with a Y-TZP product.

The energy exerted on the surface by grinding may exhibit surface toughening in principle through the tetragonal-to-monoclinic phase transformation; excessive grinding by instruments with coarse abrasives or large flutes is not recommended by most



• **Figure 10-14** Schematic illustration of transformation toughening of a yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramic.



• **Figure 10-15** Cross-section of a veneered crown with Lava zirconia-based core. (Courtesy 3M ESPE, St. Paul, MN.)

zirconia suppliers because deep flaws may offset any advantage presented by localized compressive stresses. A regeneration heat treatment of machined or superficially ground Y-TZP at 900 °C for 1 hour or less at 900 to 1000 °C converts the monoclinic phase within the surface back to the tetragonal phase. Thus, if veneer firing occurs after a grinding procedure, the thermal treatment can induce the reverse transformation of monoclinic to the tetragonal phase in the ground areas of the zirconia structure.

The volume increase in this case is constrained if the zirconia crystals are sufficiently small and the microstructure is strong enough to resist the resulting stresses. This material is extremely strong (flexural strength, ≈ 900 MPa) and tough (fracture toughness, K_{Ic} , ranges from 8 to 10.3 $\text{MP}\cdot\text{m}^{1/2}$). Many Y-TZP products are available in dentistry for CAD-CAM processing. These Y-TZP products fall into three groups: (1) to be milled in the green (compacted) state, (2) to be milled in a partially sintered state, and (3) to be milled in the fully sintered state.

Monolithic Zirconia

One approach to reducing the fracture susceptibility of ceramic restorations associated with weaker veneer is to use only core ceramics to make the entire restoration. Table 10-5 lists some properties of several core ceramics including a Y-TZP product

and the corresponding veneering ceramic. This method is especially useful in the most posterior areas of molar crowns where high occlusal clenching forces or parafunctional forces are applied. Although the fracture resistance of all-zirconia crowns is exceptionally high, there is the potential for undue wear of opposing enamel. Clinical studies have confirmed that properly polished monolithic zirconia does not cause excessive wear of opposing enamel. This is in contrast to glazed monolithic zirconia, which has been shown to cause excessive wear of enamel, especially after the glaze has worn off. Two other disadvantages of an all-zirconia crown are the difficulty in adjusting occlusion when significant premature contacts are present and the cutting difficulty and heat generated in removing defective crowns or when making an endodontic access opening with diamond burs.

Another disadvantage of monolithic zirconia is the opaque nature of this material. To offset this lack of translucency, manufacturers increased the yttria content with the production of 4Y-PSZ and 5Y-PSZ, where the tetragonal phase is lowered to about 75% and 50%, respectively, with the balance as cubic phases. With increase of cubic phase and their larger grain size, these zirconia materials exhibit greater translucency, thereby improving aesthetics. However, reducing the volume of the tetragonal phase leads to less transformation toughening and lower strength and fracture toughness of the zirconia. These translucent zirconia ceramics have strengths similar to lithia disilicate and are therefore indicated for single-unit restorations only.

Fracture Strength of Zirconia

For zirconia, the fracture toughness tends to increase with increasing grain size. Therefore the influence of grain size on transformation toughening is contrary to the increase in fracture strength for the small grain sizes seen in many other materials. One study of the influence of grain size on three-point bending strength and Vickers fracture toughness revealed that the fracture strength increases linearly for 3Y-TZP from 650 MPa for a 0.9- μm grain size up to 1000 MPa for a critical grain size of 1.4 μm , after which this decreases to 750 MPa for a mean grain size of 1.8 μm . The change in fracture strength is mainly

TABLE 10-5 Properties of Three Types of Core Ceramics and a Veneering Ceramic for All-Ceramic Prostheses

Property	PRINCIPAL CRYSTAL FORM			
	Leucite	Property	Zirconia (Y-TZP)	Veneering Porcelain for Y-TZP
Crystallinity (vol%)	35	70	≥97.5 (may also include crystalline HfO ₂ , Al ₂ O ₃ , Na ₂ O, SiO ₂ , and Fe ₂ O ₃ , etc.)	
Flexural strength (MPa)	85–112	215–400	900	85–110
Fracture toughness (MPa·m ^{1/2})	1.3–1.7	2.2–3.3	8–10.3	0.75–1.0
Vickers hardness (GPa)	5.9	6.3	8.8–11.8	4.8–5.4
Expansion coefficient (10 ⁻⁶ /K)	15.0–15.4	9.7–10.6	10.0–11.0	9.8
Elastic modulus (GPa)	65–86	95–103	210	65
Chemical durability* (μg/cm ²)	100–200	30–50	30	10–20

Y-TZP, yttria-stabilized tetragonal zirconia polycrystal.
 *International Organization for Standardization (ISO) 6872.

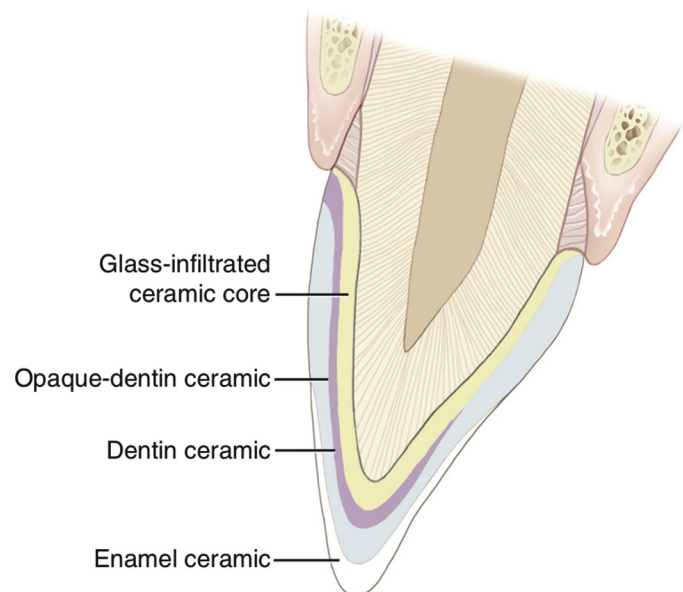
governed by the change in fracture toughness for the grain size between 0.9 and 1.8 μm. However, this relationship probably does not apply to nanocrystalline (~100-nm grain size) zirconia used in dentistry because the mean grain size is much smaller than the extrinsic defects, such as cracks caused by grinding. Thus the dependence of fracture strength on grain size should be small for dental CAD-CAM zirconia. The decrease in strength caused by very large grain sizes is likely caused by premature transformation, which causes microcracking. Kosmač et al. reported that grinding reduced the monoclinic content and the flexural strength of fine-grained zirconia, but grinding did not affect the flexural strength of coarse-grained zirconia. Curtis et al. reported that grinding with coarse-grit burs decreased the flexural strength of zirconia, but grinding with fine-grit burs did not cause a statistically significant change. Other studies listed in the reference section may present conflicting results because of differences in the initial microstructure, composition, particle-size distribution, maximum flaw sizes, and flaw-size distribution.

Hydrothermal Degradation

The long-term performance of Y-TZP may be compromised by this material's susceptibility to hydrothermal degradation. Although hydrothermal effects have been generally reported between 200 and 400 °C, longer exposure times at oral temperatures may also degrade zirconia, resulting in increased surface roughness, fragmented grains, and microcracks. The degradation process is initiated by a transformation of the surface to the monoclinic phase, which spreads through the surface grains and into adjacent grains by stresses that develop during this process. The controlling mechanism is unknown, although OH⁻ groups are thought to be responsible for breaking the atomic bonds at the surface, which produces residual stresses and the initial transformation from the tetragonal to monoclinic phase.

Glass-Infiltrated Core Ceramics

To minimize sintering shrinkage and to ensure adequate fit of ceramic prostheses, three **glass-infiltrated core ceramic** systems have been developed, one based on partially sintered alumina, one based on a magnesia-alumina **spinel** (MgAl₂O₄), and one with a zirconia-alumina core. Each of these partially sintered ceramics



• **Figure 10-16** Cross-sectional illustration of an In-Ceram crown with a glass-infiltrated core ceramic.

can be infiltrated with a lanthanum glass without any significant dimensional change.

VITA In-Ceram Alumina contains approximately 85 vol% of alumina. The partially sintered framework is formed by a slip-casting process, which produces dense packing of particles against a porous die. After firing at 1120 °C for 10 hours or more, a partially sintered structure is formed. This porous core ceramic framework is then infused with molten lanthanum glass. A schematic illustration of a cross-section of an In-Ceram Alumina crown is shown in [Figure 10-16](#).

The same type of process can also be applied to In-Ceram Spinel (ICS), which is a magnesia alumina spinel (MgAl₂O₄) core ceramic, and In-Ceram Zirconia. After glass infiltration, In-Ceram Spinel ceramic is more translucent than In-Ceram Alumina or In-Ceram Zirconia, but the mean strength is significantly lower (~350 MPa vs. ~600 MPa). The mean flexure strength of

In-Ceram Zirconia (~620 MPa) is only slightly greater than that of In-Ceram Alumina.

In-Ceram Zirconia, a zirconia-toughened alumina (ZTA) material, is not made from a pure zirconia core but, rather, a combination of 62 wt% alumina, 20 wt% zirconia, and ~18 wt% infiltrated glass. In-Ceram Zirconia is indicated primarily for crown copings and three-unit anterior and posterior frameworks when in a glass-infused form. Because there is no shrinkage associated with this process, the marginal adaptation is expected to be comparable to that of the hot-pressing method. As with 3Y-TZP zirconia, ZTA is subject to transformation toughening with conversion from tetragonal to monoclinic phases in areas where stress is induced. The result of this process is that the strength of ZTA is doubled, and the toughness is increased two to four times. The properties of alumina, ZTA, and 3Y-TZP are summarized in Table 10-6. The ZTA properties are based on an 85% alumina-15% zirconia product (ZTA-96, Astro Met, Inc., Cincinnati, OH).

Alumina Core Ceramic

Procera AllCeram (Nobel Biocare) is an alumina-core ceramic that is indicated for anterior and posterior crowns. To produce these crowns, a die is first produced from an impression and digitized

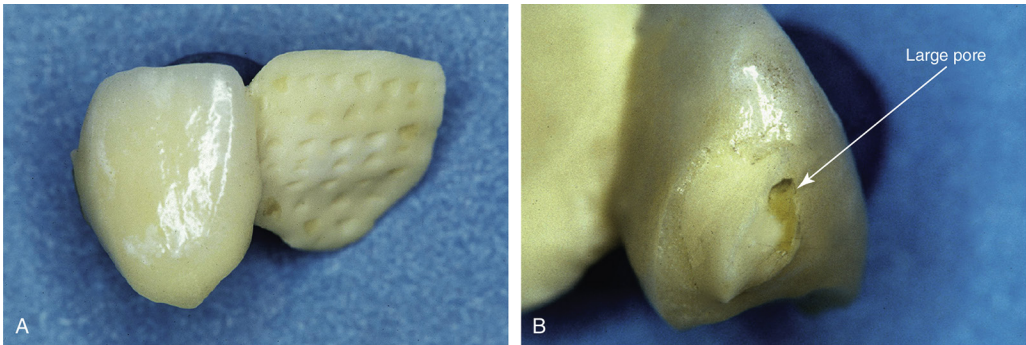
using a mechanical profiling device; then a computer converts the coordinates of the die surface into a digital database. An oversized die is then produced onto which pure alumina is dry-pressed. The oversize green alumina body is then sintered, and the resulting shrinkage yields the desired size and shape onto which a feldspathic porcelain veneer is applied and sintered. The Procera All-Ceram core is more translucent than In-Ceram Zirconia and has comparable strength (620–700 MPa). Because alumina cannot be acid-etched to produce micromechanical retention, the surface is sandblasted with silica-coated alumina particles by a Rocatec system (3M ESPE Minneapolis, MN), which is required to ensure sufficient resin bonding. Figure 10-17, A shows a fractured three-unit alumina-based bridge whose retentive flanges were dimpled to promote micromechanical bonding. The fracture surface in Figure 10-17, B shows a relatively large void that may have contributed to the fracture.

Bonding of Resin to Dental Ceramics

Bonding to prosthetic ceramics is important for three reasons: (1) resin-based composite cements are believed to increase the retention of all-ceramic prostheses, (2) resin-based composite cements are believed to increase the fracture resistance and survivability of ceramic restorations, and (3) resin-based composite

TABLE 10-6 Physical Properties of Alumina, Zirconia-Toughened Alumina, and 3Y-TZP			
Property	Alumina	Zirconia-Toughened Alumina (ZTA)	Zirconia (Y-TZP)
Density (g/cm ³)	3.95	4.10	6.07
Vickers hardness (VHN; GPa)	1175; 11.5	1750; 17.2	1300; 12.8
Flexural strength (MPa)	330	760	≥900
Average grain size (μm)	1–5	1.5	≤0.5
Modulus of elasticity (GPa)	300	310	200
Poisson's ratio	0.25	0.26	0.30
Fracture toughness (MPa·m ^{1/2})	3.5	5–7	9–13
CTE (10 ⁻⁶ /K)	8.1	8.1	10.3
Thermal conductivity (W/m·K)	24	21	2.5–2.8

CTE, coefficient of thermal expansion; 3Y-TZP, 3 mol% Y₂O₃ tetragonal zirconia polycrystal; Y-TZP, yttria-stabilized tetragonal zirconia polycrystal.



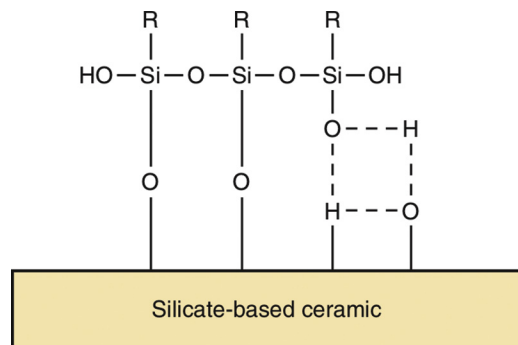
• **Figure 10-17** Fractured connector of a three-unit resin-bonded bridge made with an alumina core ceramic. **A**, Dimples on the retaining flange indicating poor wetting of the adhesive. **B**, A void within the connector to the other flange.

is the material of choice for repair of chipped or fractured core or veneer ceramic. However, silane-based coupling does not bond chemically to all ceramics. For example, as previously shown in Figure 10-17, the framework of the fractured resin-bonded bridge made with an alumina framework could not be etched. The dimpled area on one of the retained flanges of the bridge suggests that macromechanical bonding to the resin cement had been chosen. The clean separation of this framework from the resin-based cement indicates inadequate bonding. In addition, examination of the fractured flange indicates the presence of a large void that may have contributed to the fracture of the connector.

The mechanism of silane-based primer bonding to a silica network of silica-based ceramics is well known. In addition, abrasive blasting and acid-etching of the glass matrix of these ceramics create surface irregularities that can further enhance the retention of the resin cement. The penetration of the adhesive resin into the macroscopic irregularities, combined with chemical bonding, may also inhibit water access to the ceramic surface, thereby enhancing the durability of bonded ceramic prostheses. Furthermore, acid-etching can blunt the tips of microcracks within the ceramic surface. This blunting process reduces the stress concentration at the crack tips. If any voids are trapped within the interface between the crown and cement in the occlusal area, occlusal loads above this site can generate tensile stresses in the ceramic that may cause crack formation or fracture.

Silane primers or coupling agents have dual functionality, including an unsaturated group for polymerizing to adhesive resins and resin-based composites and methoxy groups ($-\text{OCH}_3$) that are hydrolyzed to silanols ($\text{Si}-\text{OH}$) for bonding to inorganics such as silica-based ceramics or metal oxide substrates through the formation of siloxane ($-\text{Si}-\text{O}-\text{Si}-$) bonds or ($-\text{Si}-\text{O}-\text{M}-$) bonds on other metal oxide substrates. Silane primers provide covalent bonds that promote adhesion at the interface between polymers and hydrolytically stable silica-based substrates, assuming that the substrate is free of contaminants. Figure 10-18 shows a schematic illustration of the bonding stage of silane primer or adhesive to a silica-based ceramic.

The reaction of silanes with silica-based ceramics involves four stages: hydrolysis, condensation, hydrogen bonding, and bond formation. After hydrolysis of the methoxy groups, condensation to oligomers occurs, and the oligomers then hydrogen bond with $-\text{OH}$ groups of the substrate. Then, during curing, covalent links are formed with the substrate, with simultaneous loss of water. These reactions typically occur simultaneously after the initial hydrolysis stage.



• **Figure 10-18** Schematic illustration of silane bonding to silica-based ceramic.

Although a monolayer of silane-based primer is preferred, multilayer adsorption generally occurs. Estimated thicknesses from deposition of a 0.25% silane solution onto glass range from three to eight molecular layers. Kitayama et al. reported that silane-based monomers produced the best bonding to silica-based ceramic, and monomers that are based on either phosphate ester or phosphonic acid monomers produce better bonding to zirconia. These bonding mechanisms are described in Chapter 6, *Mechanisms of Adhesion and Primers*.

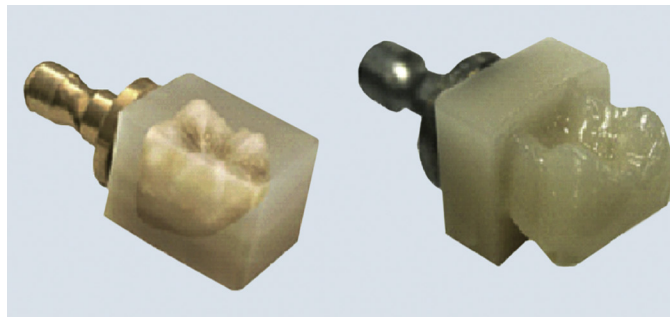
CRITICAL QUESTIONS

What causes stress concentrations? How can they promote the fracture of all-ceramic prostheses even in the presence of low occlusal forces?

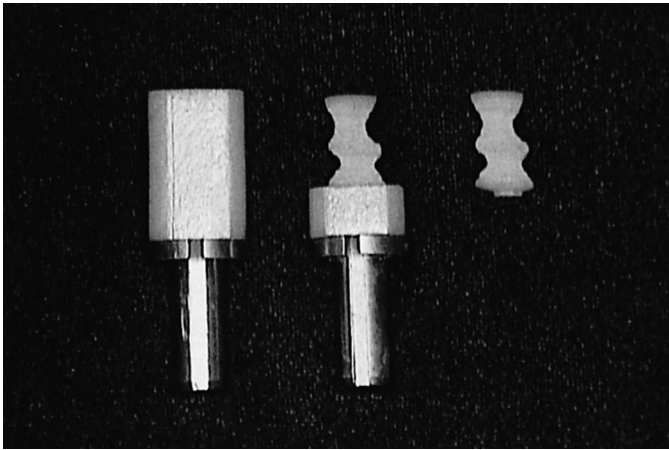
CAD-CAM Processing of Ceramics

Computer-aided milling of metals, composites, and ceramics is now possible because of advances in imaging devices, software, and CAD-CAM milling systems. **CAD-CAM ceramic** prostheses can be produced either as monolithic lithia disilicate glass-ceramic or zirconia ceramic structures or as bilayer structures made from milled copings and layered manually, by hot pressing or by fusing a CAM-produced veneer to the framework (CAD-on method). A ceramic veneer that is pressed on metal is referred to as the press-on metal (POM) method. CAD-CAM prostheses can be produced either by industrial milling processes or by chairside milling units. The industrial CAD-CAM systems are very expensive, with typical costs in excess of several hundred thousand USD. However, they are capable of processing multiple jobs with a high level of accuracy and reproducibility. Chairside systems are limited in their processing speed and their ability to process large cases.

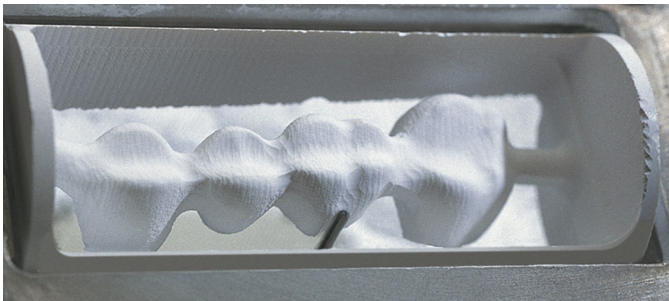
Layered zirconia prostheses can be produced from partially sintered ceramics and shaped by carbide burs to enlarged dimensions that compensate for sintering shrinkage. Fully sintered ceramics are shaped by diamond disks and burs to the precise dimensions derived from a scanned image of the prepared teeth. Typically, the external surface must be ground and polished manually, although some CAD-CAM systems are capable of milling the external surface. Figure 10-19 shows a simulated digitized image of a crown to be produced from a ceramic blank and an adjacent image of a partially milled crown. Figure 10-20 shows a Cerec ceramic block, a milled inlay form, and the final inlay.



• **Figure 10-19** Computer-aided design/computer-aided manufacturing (CAD-CAM) feldspathic ceramic block (VITABLOCS TriLux Forte). Simulated digitized image within the block (left). Partially milled prosthesis that was processed by the Sirona inLab CAD-CAM system (right). (Courtesy VITA Zahnfabrik, Bad Säckingen, Germany.)



• **Figure 10-20** Making prosthesis from computer-aided design/computer-aided manufacturing (CAD-CAM) block. Before milling (*left*). Intermediate stage of milling (*center*). The inlay removed from the mounting stub (*right*).



• **Figure 10-21** Cercon zirconia core ceramic after initial milling of the “green state” ceramic. (Courtesy Dentsply Ceramco, Burlington, NJ.)

As mentioned previously, zirconia ceramics can be milled in the **green state**, in the partially sintered state, or in the fully sintered state. A four-unit Cercon core ceramic framework can be milled in the green state (Figure 10-21); after simulated try-in (Figure 10-22); and after sintering, staining, and glazing the veneering ceramic (Figure 10-23). A typical procedural sequence for producing ceramic prostheses by a CAD-CAM system using partially sintered blanks is as follows:

1. Set the blank in the milling machine holder according to the manufacturer's instructions.
2. Set the enlargement factor to compensate for sintering shrinkage. The factor will vary according to the overall size of the prosthesis.
3. Insert the appropriate machining/milling tool.
4. After machining is completed, remove the framework and residual blank.
5. Cut the framework from the blank using a diamond disc.
6. Clean the partially sintered framework completely.
7. Dry the framework completely.
8. Place the framework in the isothermal hot zone of the sintering furnace.
9. Set the thermal processing conditions according to the sintering instructions for the specific product.
10. Sinter the framework to achieve optimum density.
11. After cooling, remove the sintered framework.



• **Figure 10-22** Finished fixed dental prosthesis framework made with Cercon core ceramic placed on teeth. (Courtesy Dentsply Ceramco, Burlington, NJ.)



• **Figure 10-23** Final Cercon fixed dental prosthesis with veneering ceramic and stain characterization. (Courtesy Dentsply Ceramco, Burlington, NJ.)

12. Inspect the framework for surface and subsurface flaws using fiberoptic transillumination.
13. Evaluate the framework for adequacy of wall thickness, ease of seating, and marginal fit.
14. If necessary, use a water-cooled diamond tool to perform minor adjustment corrections.
15. Rinse the framework thoroughly with water, and dry it completely.
16. Depending on the zirconia product, the framework may be used with or without a veneering ceramic. If a veneering ceramic is indicated, a transitional liner may be required prior to the application of the veneering (layering) ceramic.

Chairside milling is the ultimate goal of CAD-CAM processing. Until recently, the ability of a dentist to process his or her own ceramic prostheses was limited by the lack of skills in layering the veneering ceramic on the milled and fully sintered coping or framework. Because of the experience gained over many years with the Cerec system, many dentists are now able to fabricate inlays, onlays, and crowns from leucite-based ceramic blanks (ingots) and lithia-disilicate-based glass-ceramic blanks. Blanks with gradations of translucency and color, such as those developed for the VITABLOCS TriLux Forte (VITA Zahnfabrik) ceramic line, allow clinicians to produce single-unit finished prostheses

without the need for skills in the layering of a veneering porcelain. The weak link in all-ceramic prostheses is the relatively low fracture resistance of the veneering ceramics (Table 10-7).

The quality and precision of the more costly commercial imaging, designing, and milling systems have increased markedly since the 1980s because of advances in the software that controls these variables. Thus it is likely lab-operated CAD-CAM systems will continue to support crown and bridge needs well into the future.

A summary of the processing of the different core ceramics and their processing techniques is shown in Table 10-8.

Methods for Strengthening Ceramic Restorations

Brittleness and low tensile strength are the two principal deficiencies of ceramics. Methods of overcoming these deficiencies fall into two general categories: changing microstructures by physical or chemical means and minimizing stress concentration of prostheses by reducing inherent surface flaws and redesigning components. Physical means of strengthening brittle materials can be achieved by either the introduction of residual compressive stresses or the interruption of crack propagation through the material. These two

TABLE 10-7 Properties of Veneering Ceramics for Zirconia Core Materials

Veneering Ceramic	Cercon Ceram S	Lava Ceram	Tri-Ceram	VITA VM 9	Cerabien CZR
CTE (100–400 °C)	9.6	9.6	8.2	9.1	9.1
T _g (°C)	488	549	561	>590	561
Strength (MPa)	63 ± 8	81 ± 12	81 ± 22	96 ± 8	66 ± 5
Sintering Temperature (°C)	830	810	755	910	930

CTE, coefficient of thermal expansion.

TABLE 10-8 Methods of Processing the Ceramic Core Component of a Ceramic Prosthesis

Initial Forming Method	Examples	Initial Material Form	Second Processing Step	Subsequent Form	Final Steps
Condensation	Ceramco, VITA VMK, Duceram LFC, IPS d.Sign	Powder and mixing liquid	Sintering of core ceramic	Dense core ceramic with less than 5 vol% porosity	Veneer, glaze
Hot-pressing	IPS Empress 2, OPC 3G, Finesse Pressable	High-quality ceramic ingot	Stain only or stain and glaze (inlays), or veneering ceramic	Stained/glazed inlay or veneered core	Stain and/or glaze for crowns and FDPs
Casting	Dicor (Obsolete)	Glass core	Crystallization heat treatment (ceramming)	Glass-ceramic core containing a glass phase and tetrasilicic fluormica crystals	Shading porcelain (obsolete)
Slip-casting	In-Ceram Alumina, In-Ceram Spinel, In-Ceram Zirconia	Powder and mixing liquid	Partial sintering	Partially sintered core	Glass infiltration, trimming of excess glass, veneer, glaze
Computer-aided milling of fully sintered form	Cerec VITABLOCS In-Denzir BruxZir	High-quality ceramic ingot	Margin repair (if necessary)	High-quality core possibly with repaired margin	Veneer, glaze (except for BruxZir)
Computer-aided milling of partially sintered form	Cercon Lava e.max ZirCAD	Partially sintered ceramic block	Final sintering of machined/ground core and margin repair (if necessary)	Fully sintered core possibly with repaired margin	Veneer, glaze
Copy-milling	Variety of ceramic products	High-quality ceramic block	Margin repair (if necessary)	High-quality core possibly with repaired margin	Veneer, glaze
Machining, grinding of dry-pressed powder on enlarged die	Procera AllCeram	Dry-pressed and machined alumina block	Sintering	High-quality core containing 99.9% alumina	Veneer, glaze

Slip-casting, forming “green” ceramic objects by applying a slurry of ceramic particles to a porous substrate and thereby allowing capillary action to remove liquid to densify the objects before firing.

Copy-milling, the process of tracing the surface of a resin prosthesis pattern, which is then replicated on a blank of ceramic of improved physical by milling before receiving aluminous porcelain veneer.

strategies for strengthening brittle materials and specific methods based on these strategies are discussed next.

Minimizing the Effect of Stress Concentrations

Why do dental ceramic prostheses fail to exhibit the strengths that we would expect from the high interatomic bond forces? The answer is that numerous minute scratches and other flaws are present on the surfaces of these materials. These surface flaws behave as sharp notches whose tips may be as narrow as the spacing between several atoms in the material. Under intraoral loading, the tensile stresses that develop within the ceramic structure are greatly increased and concentrated at the tips of these flaws. The stress concentration geometry at the tip of each surface flaw can increase the localized stress to extremely high levels even though the average stress that exists throughout the bulk of the structure is relatively low. When the induced localized tensile stress exceeds the nominal strength of the material structure, the bonds at the notch tip rupture, forming a crack. There are other variables that affect the magnitude of these stresses and microcrack stability, including prosthesis design, load orientation, loading rate, microstructure, and residual processing stresses. These variables are discussed in other chapters.

Discontinuities in ceramic structures and in other brittle materials can cause a stress concentration in these areas. The design of ceramic dental restorations should be carefully planned with sufficient bulk and a minimum of sharp angular changes to avoid stress raisers in the ceramic. Abrupt changes in shape or thickness in the ceramic contour can act as stress raisers and make the restoration more prone to failure. For example, the incisal line angles on an anterior tooth prepared for a ceramic crown should be well rounded, and the amount of occlusal reduction for molar teeth should provide sufficient bulk for the ceramic product under consideration. [Figure 10-24](#) shows an MC pontic that has fractured because of a high stress concentration at the incisal edge. Even though an MC restoration is generally more fracture resistant than most ceramic crowns of the same size and shape, care must be taken to avoid subjecting the porcelain in an MC prosthesis to loading that produces large localized stresses. If the occlusion is not adjusted properly on a porcelain surface, contact points rather than contact areas will greatly increase the localized stresses in the



• **Figure 10-24** Porcelain debonding from a metal pontic substrate of a long-span metal-ceramic bridge.

porcelain surface and within the internal surface of the crown. These contact stresses can lead to the formation of the so-called Hertzian cone cracks that often lead to chipping of the occlusal surface. A small particle of porcelain along the internal porcelain margin of a crown also induces locally high tensile stresses. A stray particle that is fused within the inner surface of a shoulder porcelain margin of an MC crown can cause localized tensile stress concentrations in porcelain when an occlusal force is applied to the crown.

As the crack propagates through the material, the stress concentration is maintained at the crack tip unless the crack moves completely through the material or until this crack meets another crack, a pore, or a crystalline particle, which may reduce the localized stress. The removal of surface flaws or the reduction of their depth and number can produce a very large increase in strength. Reducing the depth of surface flaws in the surface of a ceramic is one of the reasons that polishing and glazing of dental porcelain is so important.

CRITICAL QUESTION

True or false? Residual compressive stress develops in the veneering ceramic of an all-ceramic crown in the same way as it does in an MC crown.

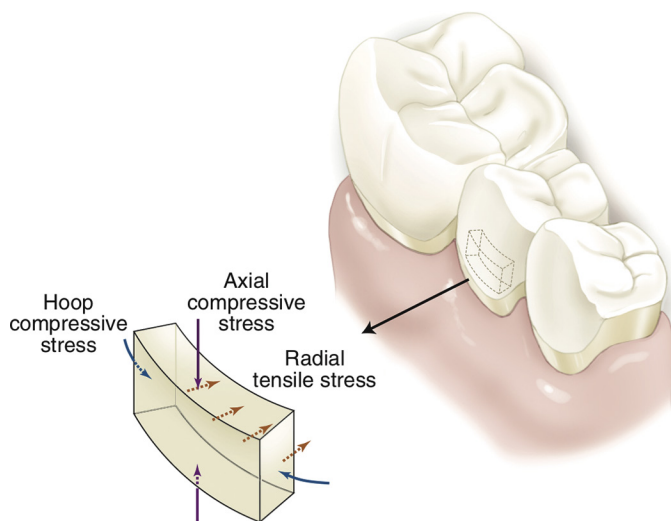
Maximize Development of Residual Compressive Stresses

Recall that when an MC prosthesis is cooled from the sintering temperature, the metal and veneering ceramic contract at different rates because of differences in their thermal contraction coefficients. Meanwhile, the chemical bond between the metal and the porcelain prevents the two components from separating; this condition forces the two components to adjust their respective dimensions at the interface as the MC cools. The adjustment of dimension results in stresses evolved at the interface. The instantaneous stress at a given temperature during the cooling cycle is termed *transient stress*, and the stress distribution, which exists at room temperature, is called the *residual stress*. Keep in mind that the materials adjacent to the interface are also under stresses but to a lower level away from the interface. In an earlier discussion, we called an MC system **thermally compatible** when the residual stress developed is insufficient to cause separation or immediate cracking of the porcelain or delayed cracking after cooling to room temperature. However, the type of stress developed in the ceramic component is of concern. Because ceramic is weak in tensile strength, the presence of any residual tensile stress within the ceramic will make the ceramic fracture at a lower stress level. In other words, the residual stress within the ceramic should be compressive.

Additional methods of introducing residual compressive stress near the surface of ceramics without using several materials of different CTE, such as ion exchange and thermal tempering, are also discussed in the following section.

Coefficient of Thermal Expansion Mismatch

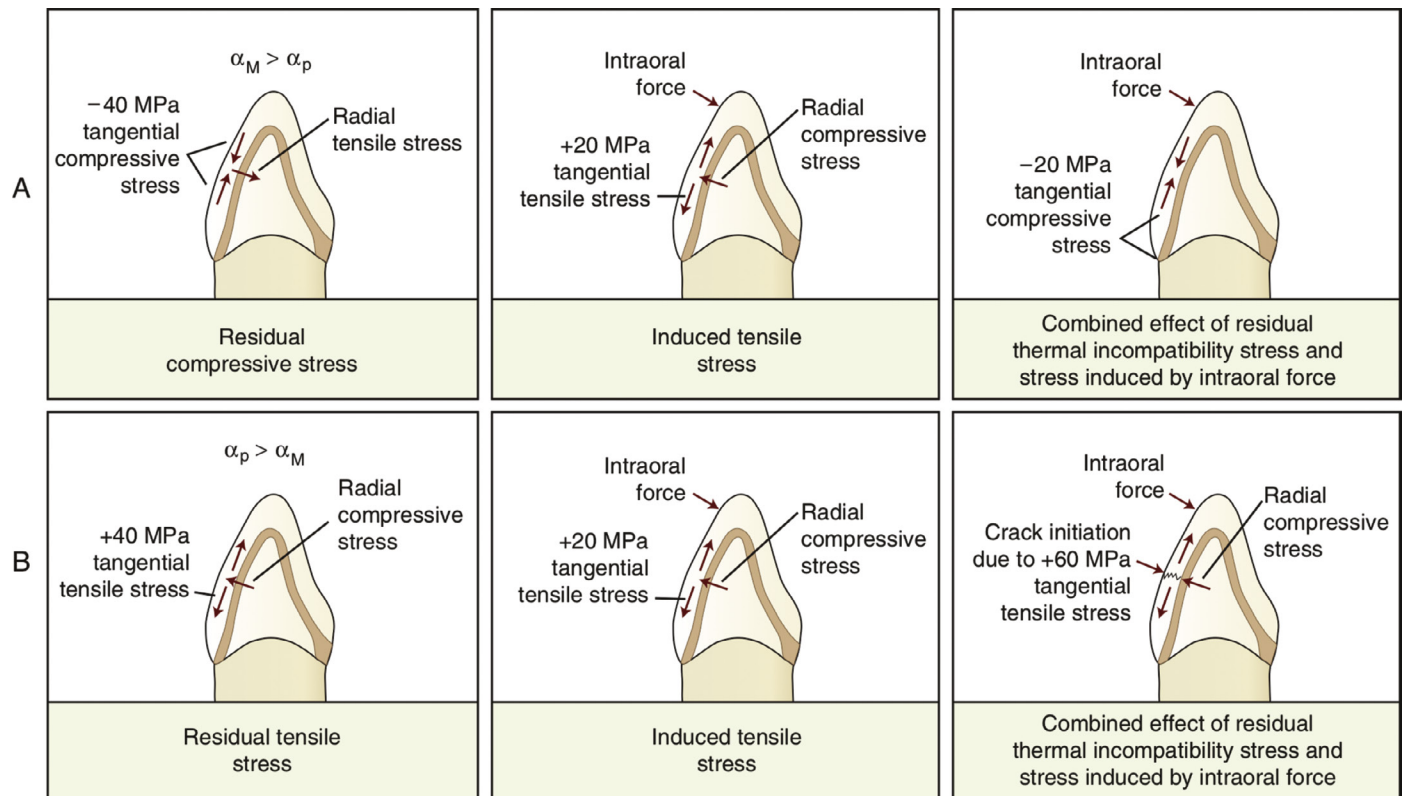
As discussed earlier, a slightly higher contraction of the metal can induce a residual compressive stress in the ceramic component when MC is cooled to room temperature. [Figure 10-25](#) shows that the ceramic component is under compression in the hoop and axial (tangential) directions but pulled in the radial direction toward the metal coping by a tensile stress. [Figure 10-26](#) shows a two-dimensional (axial and radial axes) illustration of the



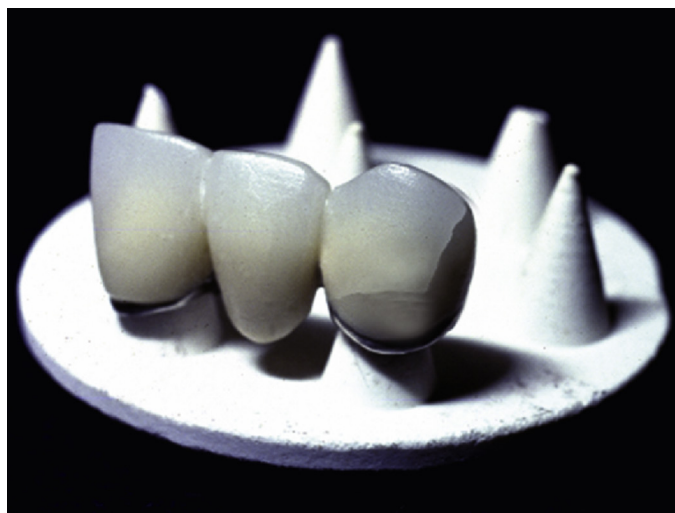
• **Figure 10-25** Residual stress in the porcelain veneer of a metal-ceramic crown for a case in which the coefficient of thermal contraction for the porcelain is less than that for the metal. The arrow pointing from the tooth to the cutout slab does not represent a stress but the projection of the area from within the prosthesis.

additive effects of tangential tensile stress (+20 MPa) induced in the porcelain veneer by intraoral forces and residual stress produced by thermal contraction differences. Assuming that the coefficient of thermal expansion of metal is greater than that of porcelain ($\alpha_m > \alpha_p$), and that there is a residual compressive stress of -40 MPa, the combined effect is -20 MPa of tangential compressive stress (Figure 10-26, A). Note that the residual compressive stress in the tangential direction actually increases the “effective” tensile strength of porcelain because this net compressive stress (-20 MPa) must first be overcome before tensile stress can develop by the applied intraoral force on the facial surface of porcelain. The residual compressive circumferential (hoop) stress (Figure 10-25) should increase the fracture resistance of the MC bond as the residual compressive tangential stress does.

Conversely, a thermal contraction mismatch that results from a higher coefficient of contraction of porcelain ($\alpha_p > \alpha_m$) will introduce residual tangential and hoop tensile stresses. That means the resistance of the porcelain to tensile failure is reduced by as much as the residual tensile stress. The additive effect of tangential tensile stress induced in the porcelain by the intraoral force can exceed the tensile strength of the porcelain and cause crack propagation in the porcelain veneer (Figure 10-26, B). When the contraction coefficient of the porcelain is much lower than that of



• **Figure 10-26** Combined effect of residual metal-ceramic incompatibility stress and intraorally induced stresses. Negative values represent compressive stress, and positive values represent tensile stress. **A**, Thermally compatible metal-ceramic system $\alpha_m > \alpha_p$, in which a residual compressive tangential stress of -40 MPa results in the ceramic veneer. An induced intraoral tensile stress of +20 MPa results in a combined stress of -20 MPa. **B**, Thermally incompatible metal-ceramic system $\alpha_p > \alpha_m$, in which a residual incompatibility tensile stress of +40 MPa is produced in the ceramic veneer. An induced intraoral tensile stress of +20 MPa results in a combined stress of +60 MPa and the formation of a crack within the ceramic.



• **Figure 10-27** Crack in metal-ceramic crown after cooling of a three-unit bridge.

the metal, porcelain cracking or MC bond failure can occur near the metal–porcelain interface (Figure 10-27). This incompatibility failure is likely caused by the development of radial tensile stresses that exceed the tensile strength of porcelain.

The principle of strengthening by thermal expansion mismatch can also be applied to all-ceramic systems. One method is to choose veneering ceramics whose thermal expansion or contraction coefficient is slightly less than that of the core ceramic. Consider three layers of porcelain, the outer two of the same composition and coefficient of thermal contraction and the inner layer of a different composition with a higher coefficient of thermal contraction. Suppose that the layers are bonded together, and the bonded structure is allowed to cool to room temperature. The inner layer has a higher coefficient of thermal contraction and tends to contract more on cooling. Thus on cooling to room temperature, the inner layer produces axial and hoop compressive stresses in the adjacent outer layer. The ability to produce this protective compressive stress to the ceramic structure before the crown is cemented to prepared teeth should increase the fracture resistance and survival probability of the prosthesis.

Ion Exchange

The technique of ion exchange is an effective method of introducing residual compressive stresses into the surface of a ceramic. If a sodium-containing glass article is placed in a bath of molten potassium nitrate, potassium ions in the bath exchange places with some of the sodium ions on the surface of the glass article and remain in place after cooling. Because the potassium ion radius is about 35% larger than that of the sodium ion, the diffusion of the potassium ion into the place formerly occupied by the sodium ion causes crowding of atoms on the surface, creating residual compressive stresses on the surface. Increases of 100% or more in the flexural strength of feldspathic porcelains have been achieved with several ion-exchange products that contain a significant concentration of small sodium ions. However, the depth of the compression zone is less than 100 μm . Therefore this strengthening effect could be lost if the porcelain or glass-ceramic surface is ground, worn, or eroded by long-term exposure to certain inorganic acids.

Thermal Tempering

Perhaps the most common method for strengthening glasses in general usage is by thermal tempering. Thermal tempering creates residual surface compressive stresses by rapidly cooling (quenching) the surface of the object while hot and in the softened state. This rapid cooling produces a skin of rigid glass surrounding a soft core. As the softened core solidifies, the core tends to shrink, but the outer skin remains rigid. The pull of the hardening core on the outer skin during shrinking generates residual compressive stresses within the outer surface while the core experiences residual tensile stresses.

Thermal tempering is used to strengthen glass for uses such as automobile windows and windshields, sliding glass doors, and diving masks. A more effective approach for dental applications is quenching hot glass-phase ceramics in a silicone oil bath or other special liquids. This thermal tempering treatment induces a protective region of compressive stress within the surface. However, this process is technique sensitive because large counterbalancing tensile stresses may develop when excessive cooling rates occur during the tempering process.

Interruption of Crack Propagation

When we discuss the fracture of an object, we often attribute the cause to crack propagation. Thus stopping, impeding, or redirecting the crack propagation can prevent or delay fracture until a greater external force is applied. The increase in stress to fracture an object is the result of strengthening. There are two approaches to interrupting crack propagation, as discussed next.

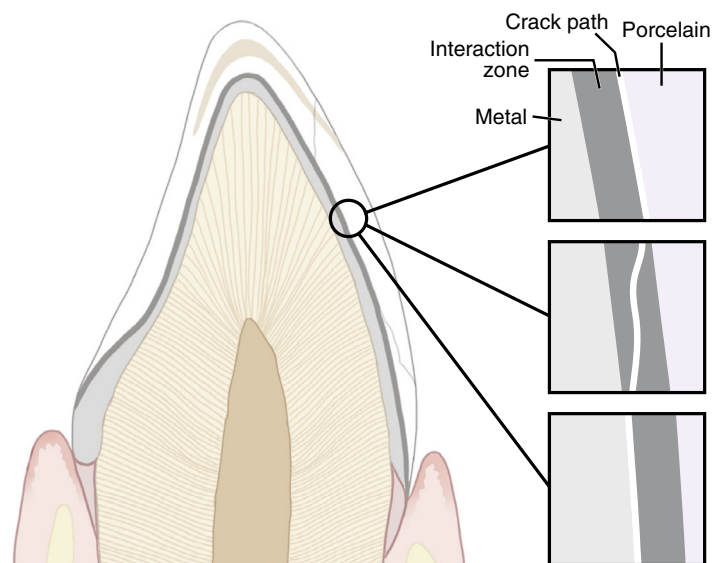
Crystalline Particle Strengthening

Reinforcement of ceramics with a dispersed phase of a different material can prevent or inhibit the propagation of cracks. This process is referred to as *dispersion strengthening*. When small, tough crystals are homogeneously distributed in a glass, the ceramic structure is toughened and strengthened because cracks cannot penetrate the fine particles as easily as through the glass. This technique was applied decades ago in the development of aluminous porcelains (in which Al_2O_3 particles were dispersed in a glassy porcelain matrix) for all-porcelain crowns. Most current dental veneering ceramics have a glassy matrix that is reinforced by a dispersed crystal phase. Glass matrices in dental ceramics have been strengthened and toughened by a variety of dispersed crystalline phases, including leucite, lithia disilicate, alumina, and tetrasilic fluormica.

Almost all modern higher-strength ceramics derive their improved fracture resistance from the crack-blocking ability of crystalline particles. Hot-pressed core ceramics and veneering glass-ceramics contain a glass phase that is strengthened with crystalline particles of leucite, lithia disilicate, alumina, magnesia-alumina spinel, and other types of crystals. Toughening depends on the crystal type, crystal size, volume fraction, interparticle spacing, and CTE relative to the glass matrix. For example, the fracture toughness (K_{Ic}) of soda-lime-silica glass is $0.75 \text{ MPa}\cdot\text{m}^{1/2}$. If one disperses approximately 34 vol% of leucite crystals in the glass, such as in IPS Empress, K_{Ic} increases only to $1.3 \text{ MPa}\cdot\text{m}^{1/2}$. However, by dispersing 70 vol% of interlinked lithia disilicate crystals in a glass matrix, such as in IPS e.max Press, K_{Ic} increases to $3.3 \text{ MPa}\cdot\text{m}^{1/2}$.

Transformation Toughening

In contrast to dispersion strengthening, the ability of a material to undergo a stress-induced transformation that hinders crack propagation is known as *transformation toughening*. A good example is tetragonal zirconia polycrystals in zirconia-based dental ceramics



• **Figure 10-28** Cross-sectional illustration of interfacial zone fracture: ceramic-metal oxide (*top*), trans-metal oxide (*middle*), and metal-metal oxide (*bottom*).

that undergo a transformation into a stable monoclinic crystal upon the impact of growing microcracks. A detailed discussion is presented in the section of Stabilized Zirconia.

Summary

The fracture resistance of ceramic prostheses can be increased through one or more of the following six options: (1) select stronger and tougher ceramics; (2) develop residual compressive stresses within the surface of the material by thermal tempering; (3) develop residual compressive stress within interfacial regions of weaker, less tough ceramic layers by properly matching coefficient of thermal expansion; (4) reduce the tensile stress in the ceramic by appropriate selection of stiffer supporting materials (greater elastic moduli); (5) design the ceramic prosthesis with greater bulk and broader radii of curvature to minimize the magnitude of tensile stresses and stress concentrations during function; and (6) adhesively bond the ceramic crowns to tooth structure.

CRITICAL QUESTION

Which processing technique is most likely to generate the deepest flaws in a ceramic core framework?

Effect of Design on Fracture Susceptibility of Metal-Ceramic and All-Ceramic Restorations

There are many examples of atypical designs that lead to ceramic fracture of MC restorations. Tougher, stronger ceramics can sustain higher tensile stresses before cracks develop in areas of tensile stress. Conventional feldspathic porcelains should not be used as the core of ceramic crowns, especially in posterior areas, because occlusal forces can easily subject them to tensile stresses that exceed the tensile strength of the core ceramic. Because the forces on anterior teeth are relatively small, low to moderate tensile stresses can be supported by ceramic crowns more safely. However, if there is a great amount of vertical overlap (overbite) with only

a moderate amount of horizontal overlap (overjet), high tensile stresses can be produced.

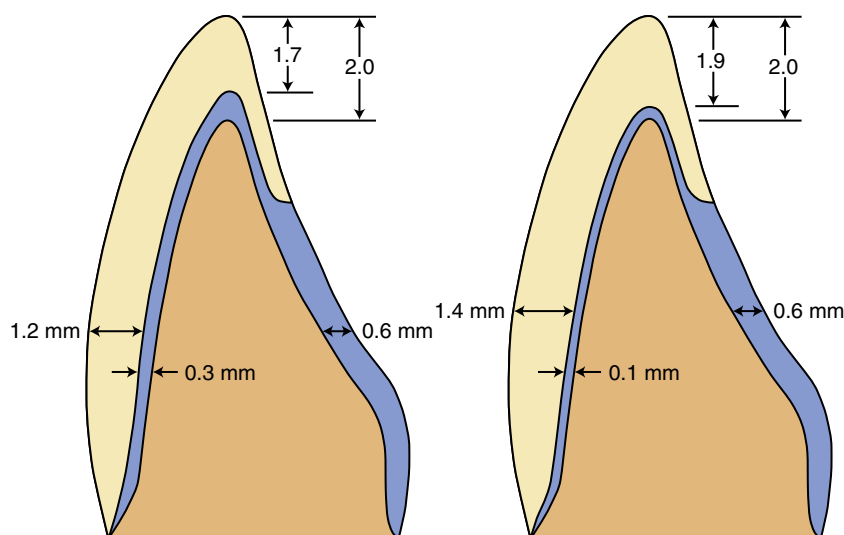
When fractures occur, a sketch of the observed fracture surface is helpful to assist in determining the cause of fracture. An illustration of the main crack patterns that can develop in an MC crown is shown in [Figure 10-28](#). Some cracks travel along the metal-metal oxide interface, and others may propagate along the interface between the metal oxide and opaque porcelain. The third type can occur cohesively within porcelain entirely. The first two types are indicative of a material processing error, and the third may be indicative of a crown design error, excessive loading, or other uncontrollable factors.

Although ceramic and MC prostheses are susceptible to design errors, some variations in design have minimal effects on the stress levels generated during loading. For example, the MC crown designs shown in [Figure 10-29](#) have quite different metal thicknesses in the facial area, yet finite-element analyses reveal no significant differences in the maximum principal tensile stresses that develop under simulated loading.

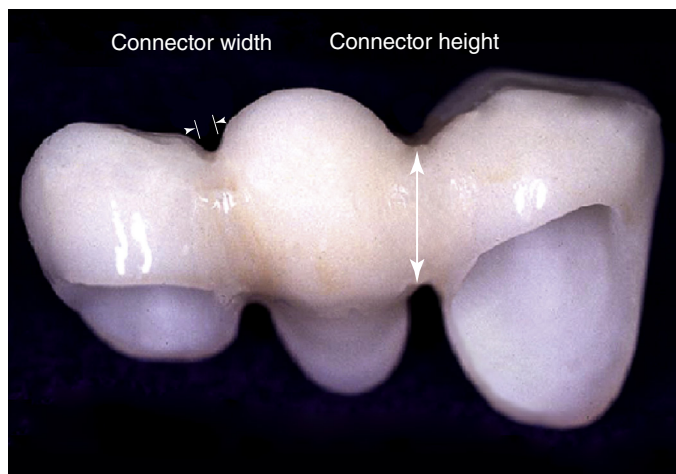
Sharp line angles in the preparation also will create areas of stress concentration in the restoration, primarily where a tensile component of bending stress develops. A small particle of ceramic along the internal porcelain margin of a crown can induce locally high tensile stresses during try-in or final cementation. Furthermore, when grinding of this surface is required for adjustment of fit, one should use the finest-grit abrasive that will accomplish the task. This precaution will reduce the probability of forming microcracks and will reduce the depth of microfissures that are produced by the abrasive particles. Grinding flaws in the inner surface of ceramic crowns represent the greatest damage that can be produced in ceramics by processing techniques.

CRITICAL QUESTION

Describe four ways by which control of tooth preparations and the design of crowns and bridges can increase the resistance to fracture of all-ceramic crowns.



• **Figure 10-29** Cross-sectional illustrations of metal-ceramic crown designs with reduced metal thickness. Metal is represented by an aqua color and porcelain by yellow. Facial metal thickness of 0.3 mm (left). Facial metal thickness of 0.1 mm represents a more aesthetic option (right).



• **Figure 10-30** Connector dimensions for a three-unit ceramic bridge.



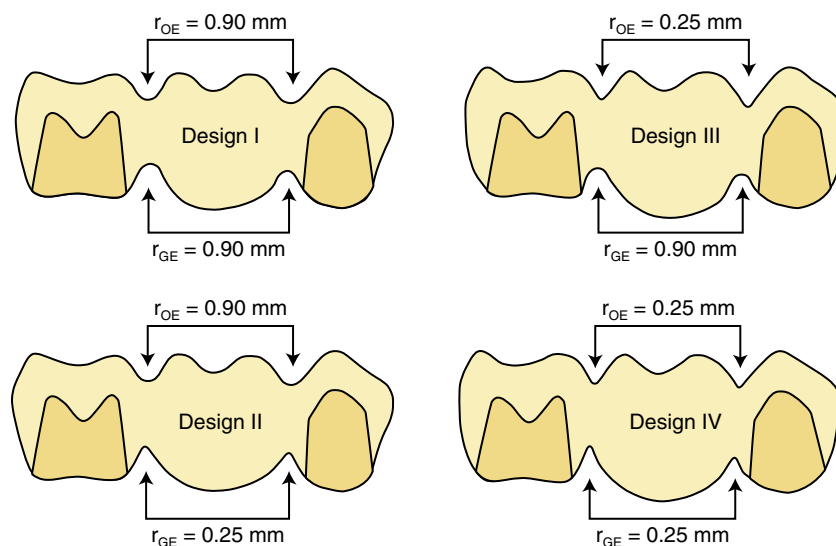
• **Figure 10-31** A three-unit ceramic anterior-posterior fixed dental prosthesis produced totally from a lithia-disilicate-based core ceramic. Note the relatively large connector (4 mm in height) necessary to resist fracture in posterior areas.

Most ceramics should be designed in such a way as to overcome their weaknesses, that is, the relatively low fracture toughness and tensile strength of veneering ceramics and their susceptibility to crack formation in the presence of surface flaws. The design should avoid exposure of the ceramic to high tensile stresses. Knife-edge margins should be avoided because of the risk of cracking or chipping during the try-in phase. The tensile stresses in a ceramic FDP can be reduced by using greater connector thicknesses (Figure 10-30) and by broadening the radius of curvature of the gingival embrasure (Figure 10-31) portion of the interproximal connector. However, a connector height greater than 4 mm in the posterior area of the mouth is often unrealistic because of shorter crowns and can result in bulky, unaesthetic connectors (Figure 10-32). Fractured connectors are fairly common, especially when the connector size is less than that recommended by the manufacturer. Figure 10-33 illustrates an example of this design deficiency. The distal connector of

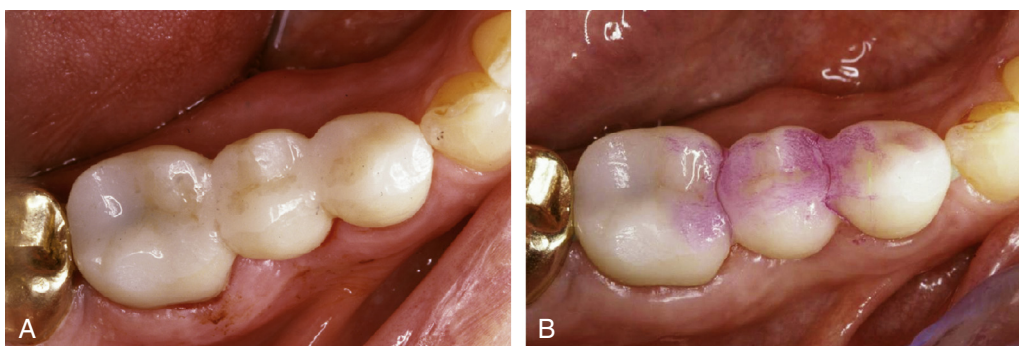
the three-unit bridge made from a lithia-disilicate core ceramic fractured after 18 months in service, and the mesial connector fractured later. The distal connector was only 3.5 mm or 0.5 mm less than was recommended. Quinn et al. studied the effect of stress concentration factor (Chapter 4, Stress Concentration) in the gingival embrasure area on the predicted minimum connector size needed for a four-unit zirconia framework to ensure a 95% survival against fracture over a period of 20 years. The results confirm the importance of geometrical features on the maximum stress and the corresponding probability of failure (Figure 10-34).

CRITICAL QUESTION

What are the indications and contraindications for the use of all-ceramic crowns?



• **Figure 10-32** Ceramic bridges with various radii of curvature in occlusal and gingival embrasures. Designs I and III have the lowest stress concentration factors in the gingival (tensile) embrasure areas, which have the larger radii of curvature.



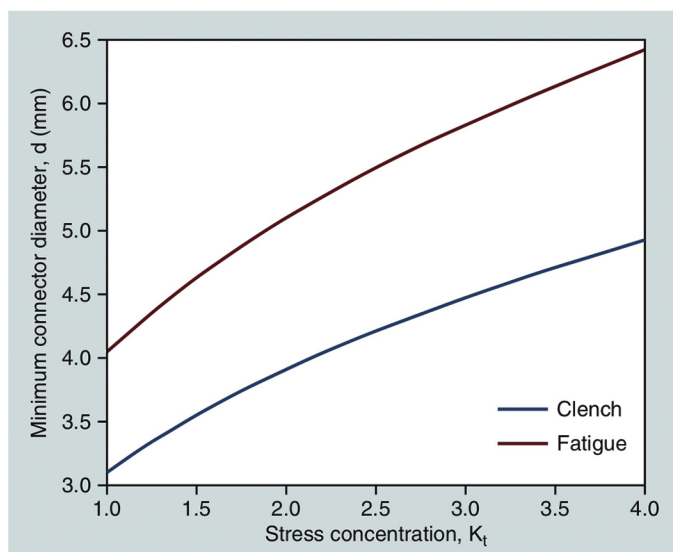
• **Figure 10-33** A, Postcementation photo of three-unit ceramic bridge made with a lithia-disilicate-based core ceramic. B, Fractured connectors of the bridge after approximately 18 months. The posterior connector height was found to be 3.5 mm, which was 0.5 mm less than that recommended by the manufacturer.

Principles for Selection of Dental Ceramics

A properly made MC crown is more fracture resistant and more durable than most all-ceramic crowns and bridges. This technology is well established compared with the technologies required for the most recent all-ceramic products. Although the biocompatibility of some metals used for copings and frameworks may be a concern for patients who have known allergies to those metals, these situations are rare. A metal coping or framework provides an advantage compared with zirconia-based ceramic prostheses when endodontic access openings through crowns are required. Temporary repairs for ceramic fractures that extend to the metal framework are possible, without the need for intraoral sandblasting treatment, by using current resin bonding agents. All-ceramic crowns can be more susceptible to chipping fracture and to bulk fracture in posterior sites. Fractures of ceramic connectors represent another disadvantage of all-ceramic prostheses, especially when the manufacturer's recommendations for connector shape and size cannot be applied. Overall, the aesthetic appearance of an all-ceramic restoration is generally superior to that of an MC

restoration for anterior and posterior situations. However, properly designed MC crowns are highly aesthetic when adequate tooth-reduction principles are satisfied. In addition, metal coping designs, such as thinner facial metal (0.1 to 0.5 mm) and/or knife-edge facial metal margins, or collarless metal margins can further enhance the aesthetic potential of these anterior crowns.

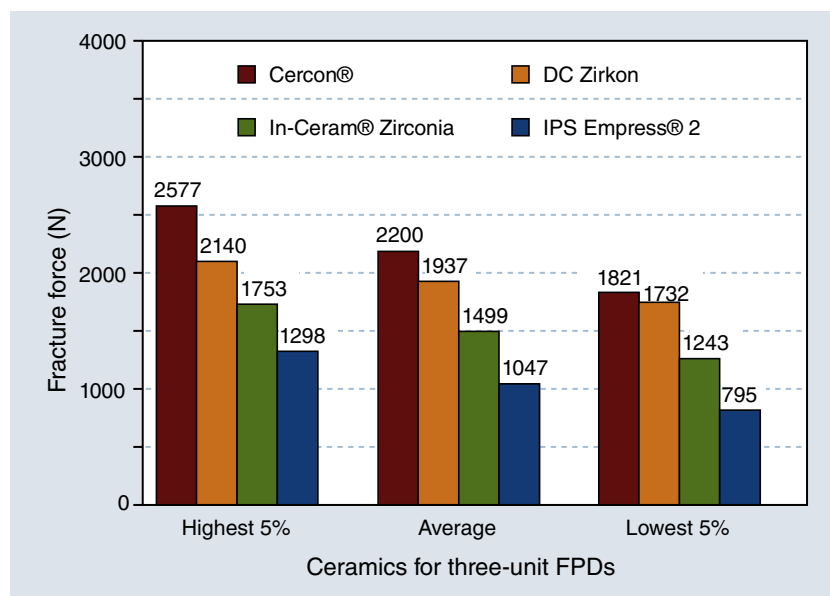
Although an all-ceramic crown exhibits superb aesthetics, some all-ceramic bridges are not as aesthetic because the connectors must be sufficiently thick to minimize the risk for fracture, or the core ceramic is excessively opaque. Some all-ceramic crowns will not be aesthetic if the tooth preparations are inadequate, particularly when insufficient tooth structure has been removed. Not all patients will benefit from the placement of all-ceramic crowns or bridges. Some individuals exhibit certain characteristics that would allow only a metal or MC bridge to be used. For example, if an individual bruxes frequently and with great force, an all-ceramic bridge would not be likely to survive. A ceramic bridge should not be placed in patients who have a long span across the pontic site because the higher stresses under function could lead to premature fracture. There are several clear indications and contraindications



• **Figure 10-34** The fatigue curve is the result of finite-element analysis showing the minimum connector diameter required for a four-unit all-ceramic bridge made from 3 mol% Y_2O_3 tetragonal zirconia polycrystal (3Y-TZP) to ensure a survival rate of 95% for at least 20 years. Other parameters used in the analysis are mastication frequency of 1400 cycles/day and maximum cyclic stress of 346 MPa. The stress concentration factor (K) is the ratio of maximum stress in the gingival embrasure area (Figure 10-34) to either the nominal or net-section stress across the connector. The clench curve shows the connector diameter needed to prevent fracture under the same stress of 346 MPa (single cycle) for comparison. (Adapted from Quinn GD, et al: Fatigue of zirconia and dental bridge geometry: design implications, *Dent Mater* 26:1133–1136, 2010.)

that should be kept in mind when treatment planning crown and bridge cases made with a ceramic system. Therefore all-ceramics are preferred over MCs when aesthetics is a prime concern, when MC aesthetics is unacceptable, or when a history of metal hypersensitivity exists. Table 10-9 lists the types of dental ceramics by their recommended indications for and contraindications against their use based in part on evidence from clinical studies. Although manufacturers and dental laboratory owners usually list the indications for use of ceramic products, they do not typically state their contraindications. Only after clinical evidence of adverse events occur do the indications change and contraindications become more clearly specified. The information presented does not guarantee success nor is it predictive of failure, because many variables are involved that may shift the balance of risk from low to high.

The toughest and strongest core ceramics have opaque cores that are veneered with layers of translucent ceramic. The prediction of the most durable ceramic should be based on the fracture resistance of the entire bilayer or trilayer system, not simply of the core ceramic itself. In the absence of randomized, controlled clinical data, in vitro tests of the monolithic ceramic materials and of layered ceramics that simulate the designs used in clinical practice are highly desirable. For example, Figure 10-35 shows the mean fracture loads across three strength ranges of three-unit bridges made using four ceramic materials. If more bridges had been tested, Weibull analyses could have been performed on the data to determine the reliability and fracture probabilities over time. More importantly, finite-element models can be developed for any prosthesis design that can be applied with dynamic fatigue data for the component ceramic materials using Life Ceramics Analysis and Reliability Evaluation software (CARES; NASA) to predict the time-dependent probabilities for fracture.



• **Figure 10-35** Average loads (N) required to fracture at midpontic of three-unit bridges made from four ceramics in which the core ceramic thickness was 0.8 mm, the veneer thickness was 0.7 mm, and the connector height was 4 mm. The differences between the weakest and strongest ceramic bridges in each grouping were 99%, 110%, and 129%, respectively. The core ceramics for the four products are as follows: Cercon and DC Zirkon-Ceram are zirconia-based ceramics, In-Ceram Zirconia is glass-infiltrated zirconia-reinforced alumina ceramic, and Empress 2 is a lithia-disilicate-based ceramic. (Adapted from Tinschert J, et al: Fracture resistance of lithium disilicate-, alumina-, and zirconia-based three-unit fixed partial dentures: a laboratory study, *Int J Prosthodont* 14:231–238, 2001.)

TABLE 10-9 General Indications and Contraindications for Use of Dental Ceramics

Type	Primary Application	Secondary Applications	Contraindications
Feldspathic porcelain	Metal-ceramic veneers Anterior laminate veneers	Single-surface inlays/low-stress sites High translucency needed	Inlays, onlays, crowns and bridges (except as metal-ceramic veneers) Bruxism
Aluminous porcelain	Core ceramic for anterior crowns	Low-stress premolar crowns	Molar crowns Bridges Bruxism
Leucite glass-ceramic	Anterior single-unit crowns Anterior laminate veneers	Low-stress premolar inlays and crowns High translucency needed	High-stress situations Bridges Bruxism
Lithia disilicate glass-ceramic	Anterior and premolar crowns Anterior 3-unit bridges Premolar crowns	Anterior laminate veneers Posterior 3-unit bridges to 2nd premolar	High-stress posterior situations Bridges involving molar teeth Bruxism
Alumina	Core ceramic for crowns Low-stress anterior bridges	Low-stress posterior bridges	Anterior veneers High-stress posterior bridges Bruxism
Glass-infiltrated spinel	Anterior crowns	High translucency needed	Anterior bridges Posterior crowns and bridges Bruxism
Glass-infiltrated alumina	Anterior and posterior crowns	Anterior bridge substructures up to 3 units	Anterior veneers Posterior crowns and bridges High translucency needed Bruxism
Glass-infiltrated alumina/zirconia	Posterior crowns Posterior bridge substructures up to 3 units	Anterior bridge substructures up to 3 units	Anterior veneers and crowns Where high translucency needed Bruxism
Zirconia (Y-TZP) (with veneering ceramic)	Posterior crowns Posterior bridge substructures up to 5 units		Anterior veneers, crowns, and bridges High translucency is needed Bruxism
Zirconia (3Y-TZP) (monolithic, without veneering ceramic)	Posterior crowns and bridges (limited clinical data available)	Posterior core-ceramic bridges	Anterior veneers, crowns, and bridges High translucency is needed Bruxism
Ce-TZP/ Al_2O_3	Posterior crowns and bridge substructures (no clinical data available)	—	Anterior veneers, crowns, and bridges High translucency is needed Bruxism
4Y-PSZ	Anterior crowns, posterior crowns, veneers, onlays		Bridges, high-stress areas
5Y-PSZ	Anterior crowns, posterior crowns, veneers, onlays		Bridges, high-stress areas

4Y-PZE, 5 mol% Y_2O_3 partially stabilized zirconia; 5Y-PZE, 5 mol% Y_2O_3 partially stabilized zirconia; 3Y-TZP, 3 mol% Y_2O_3 tetragonal zirconia polycrystal; Y-TZP, yttria-stabilized tetragonal zirconia polycrystal.

The success or failure of ceramic restorations can be related to material-, dentist-, lab-, technician-, and patient-related factors. The specific cause of failure often results from failure to follow the manufacturer's guidelines. For example, feldspathic porcelain must be supported by a metal coping or high-strength ceramic core to resist occlusal loading and prevent excessive flexural strain and should not be used as the core ceramic for a ceramic-ceramic crown. The comparative fracture toughness values of ceramics are listed in [Tables 10-5](#) and [10-6](#). Another

cause of fracture is inadequate occlusal reduction on premolar and molar teeth. A minimum of 1.5-mm reduction is recommended for MC crowns in molar areas, compared with a thickness of 2.0 mm for most ceramic crowns. However, the introduction of monolithic zirconia crowns suggests that occlusal reductions as low as 0.6 mm may be adequate in some cases. For any ceramic product, the tooth-preparation guidelines recommended by the manufacturer should be followed for the specific ceramic that will be used. These guidelines should be

discussed with the lab technician to ensure that standardized procedures are followed.

When a dentist writes a prescription for an MC or ceramic prosthesis, specific information is required on the material to be used and the design that is needed. How should these decisions be made by a competent clinician? The intraoral conditions and optimal treatment options must first be considered. For missing teeth, restoring the dentition to occlusal function may be accomplished with implants and crowns or FDPs. The aesthetic needs, expectations, and financial resources of the patient are the next criteria to be considered. The treatment choice is then made on the basis of anticipated success rates, survival times, and minimization of risk factors that are determined from published clinical studies and the previous experience of the clinician, the dental lab technician, and their colleagues. For recent dental school graduates, the previous experience is often based on the materials and techniques learned in dental school. For well-established dentists, experiences in dental practices complement their dental school and advanced education training. Although one may have developed an extensive base of experience, the decision matrix of materials, design options, techniques, experience, patient conditions, and predicted success rates represents an overwhelming combination of variables to factor into optimal treatment decision making.

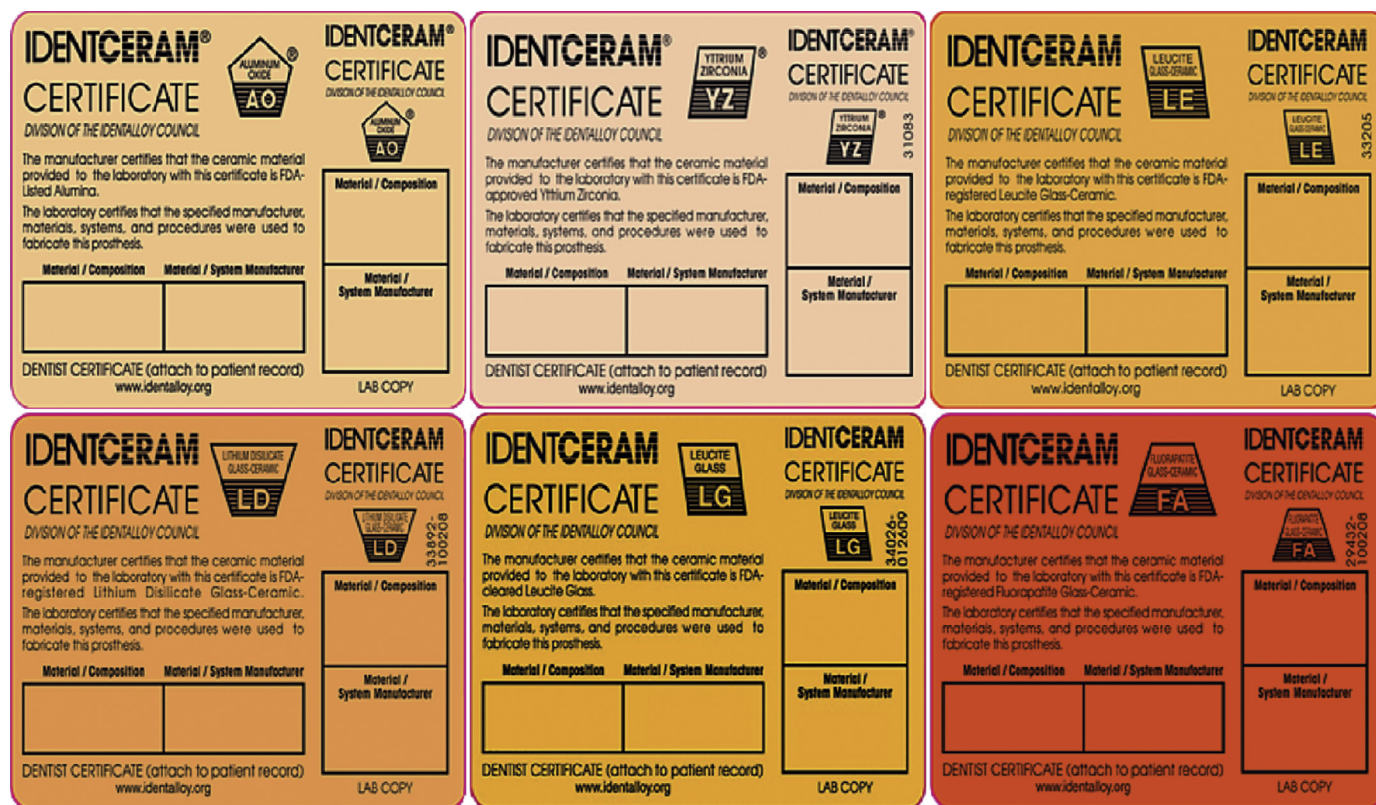
The dental literature provides convincing evidence that the most durable types of posterior prostheses are those produced from high-noble alloys, particularly gold-based alloys. However, the profession has entered an aesthetics-oriented phase in which decisions tend to favor appearance over long survival times. Thus the selection of dental materials products tends to favor the use of resin-based composites and ceramics for single-unit and multiple-unit restorations. In many cases, MC material systems are chosen

over all-ceramic systems as a compromise between aesthetic needs and minimizing the time-dependent probability of failure or maximizing survival.

The dentist and lab technician are faced with a complex challenge of deciding which ceramic should be used for each specific clinical situation. Although some products are recommended for posterior three-unit to five-unit FDPs, one should first consider the use of all-metal FDPs or MC FDPs because these prostheses will have a much greater life expectancy. Only when a patient is highly resistant to accepting metallic components during the treatment-planning discussions should all-ceramic FDPs be used because the fracture resistance of posterior all-ceramic FDPs is based on (1) the strength and fracture toughness of the ceramic components, (2) the connector dimensions (minimum height of 4 mm), (3) connector shape (gingival embrasures must have broad radii of curvature), and (4) the patient's biting force. Thus the selection of a ceramic for these prostheses is a very risky proposition because optimal conditions for their success are not yet known.

IdentCeram Certificates for Identification of Ceramic Products

IdentAlloy certificates have been used by dental labs for many years to identify alloys that are used in prosthetic cases sent by the lab to dentists. Because of the strong recent demand for all-ceramic prostheses, IdentCeram certificates were introduced in 2007 to identify the manufacturer/company, brand name, and composition of the materials used for all-ceramic prostheses. Six of the IdentCeram certificates are shown in Figure 10-36. The



• Figure 10-36 IdentCeram certificates.

letter codes are designated as follows: AO (aluminum oxide), YZ (yttrium zirconia), LD (lithia disilicate glass-ceramic), FA (fluorapatite glass-ceramic), LE (leucite glass), and LG (leucite glass-ceramic). There are newer certificates such as HC (hybrid ceramic) and ZLS (zirconia lithium silicate) not featured here. The certificates exhibit a recognizable letter code that helps ensure proper insurance coding. These codes correspond to IdentAlloy codes for high noble (HN), noble (N), and predominantly base metal (PB) alloys. By using these widely recognized certificates, labs and

dentists gain a proven, practical way to document this information in their patient charts and ensure consistent communication with their dental lab technicians.

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Full Selected Readings for this chapter can be found on www.expertconsult.com.

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11

Prosthetic Polymers and Resins

OUTLINE

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KEY TERMS

Denture liner The polymeric material used to replace the tissue-contacting (intaglio) surface of an existing denture. A denture liner may be hard or soft, short or long term.

Long-term resilient soft liner A resilient polymeric material that is bonded to the tissue-contacting surface of a denture for cushioning and/or improved retention. Such liners typically are heat-processed, and thus, they are more durable than chemical-activated, short-term soft liners and tissue conditioners.

Rebasing The process of replacing the entire denture base of an existing complete or partial denture.

Relining The process of replacing the tissue-contacting surface of an existing denture.

Resilient soft denture liner A polymeric material that is placed on the tissue-contacting surface of a denture base to absorb

some of the mastication impact energy by acting as a type of “shock absorber” between the occlusal surfaces of a denture and the underlying oral tissues. A denture soft liner may also be used to engage natural or prosthetic undercuts so as to provide retention, stability, and support. These materials may be placed chairside (directly) or in the dental laboratory (indirectly).

Short-term soft liner (tissue conditioner) A resilient polymeric material that is employed for brief periods (up to 14 days) to absorb masticatory impact and adapt to changing ridge contours (e.g., following the extraction of teeth or surgical alteration of an edentulous or partially edentulous ridge). Such materials are typically chemical-activated polymers and tend to degrade more rapidly than heat-activated resins.

The Glossary of Prosthodontic Terms, 9th edition, defines a complete denture as a removable dental prosthesis that replaces the entire dentition and associated structures of the maxilla or mandible. Such a prosthesis is composed of artificial teeth attached to a denture base. In turn, the denture base derives its support through contact with the oral tissues, teeth, or dental implants.

Although individual denture bases can be formed from metals or ceramics, the majority of denture bases are fabricated using common polymers. Such polymers are chosen based on availability, dimensional stability, handling characteristics, color, and compatibility with oral tissues.

A description of commonly used denture base polymers is presented in this chapter. Considerable attention is given to individual processing systems and polymerization techniques. In addition, methods for improving the fit and dimensional stability of resin-based prostheses are provided.

Acrylic Resins

Since the mid-1940s, the majority of denture bases have been fabricated using poly(methyl methacrylate) resins, also known as *PMMA*. PMMA is a colorless transparent solid that can be tinted with pigments, dyes, fillers, and fibers to provide almost any color, shade, and degree of translucency. The color, optical characteristics, and dimensional properties of PMMA remain stable under normal intraoral conditions, and its physical properties have proven to be adequate for dental applications.

One decided advantage of PMMA is the relative ease with which this material can be processed. PMMA denture base material is commonly supplied as a powder–liquid system ([Figure 11-1](#)). The liquid contains mostly methyl methacrylate monomers, di- or trimethacrylate crosslinking agents ([Figure 11-2](#)), and an inhibitor, and the powder contains predominantly PMMA resin in the form of micro-sized beads (or spheres). When the liquid and powder

are mixed in the proper proportions, a workable mass is formed. The material is introduced into a properly formed mold cavity and polymerized under heat and pressure. Recall from [Chapter 2, Chemistry of Polymerization](#), that polymerization can be activated by chemical, heat, and light energy. Microwave energy may also be used for polymerization. In addition, computer-aided

design/computer-aided manufacturing (CAD-CAM) technologies of milling PMMA pucks and three-dimensional (3-D) printing using methacrylate-based monomers ([Chapter 15, Additive Manufacturing—3D printing](#)) are also available.

General Technique of Denture Base Fabrication

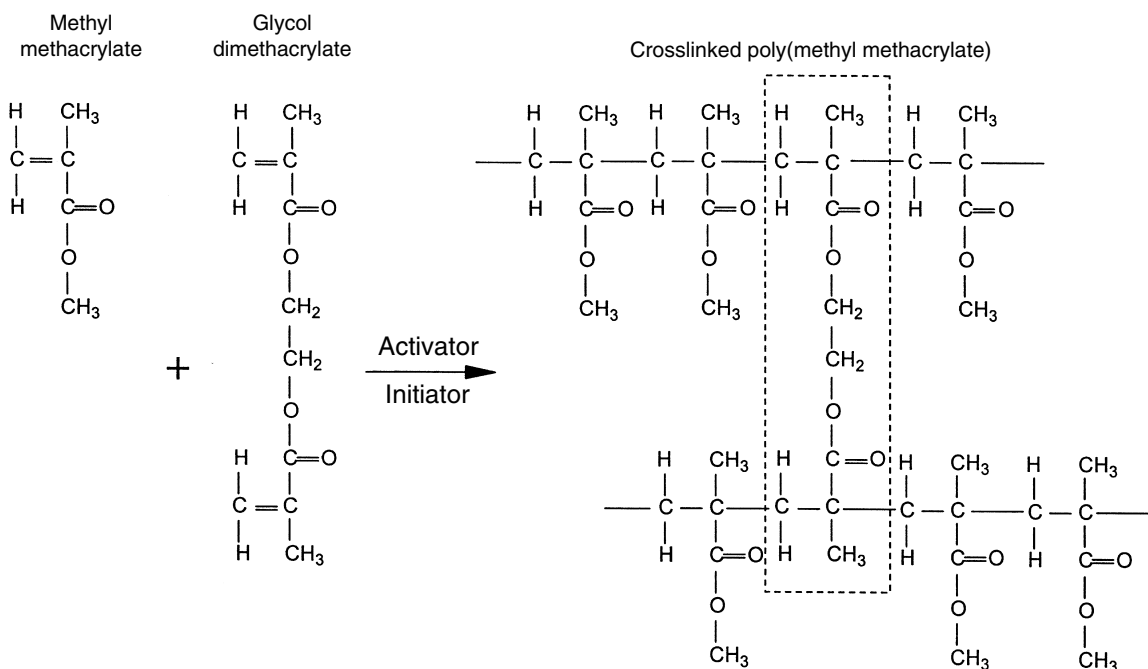
Several processing techniques are available for the fabrication of denture bases ([Figures 11-3 to 11-11](#)). Each technique requires a suitable impression of the associated dental arch, followed by the fabrication of an accurate gypsum cast. In turn, a resin record base is fabricated on the cast. Wax is added to the record base, and prosthetic teeth are related to the opposing dentition and evaluated in the patient's mouth before proceeding.

In the laboratory, a bronze denture flask is used, and the completed tooth arrangement is encased in a suitable investing medium (usually gypsum). A plastic denture flask is mandatory if microwave energy is used. Subsequently, the denture flask is opened, and the wax denture base is eliminated in a hot-water bath, leaving the prosthetic teeth in place. After a thorough cleansing of the mold, an appropriate separator is applied to the gypsum surface. In turn, a resin denture base material is introduced into the mold cavity and polymerized under pressure. Following polymerization, the denture is recovered and prepared for clinical placement.

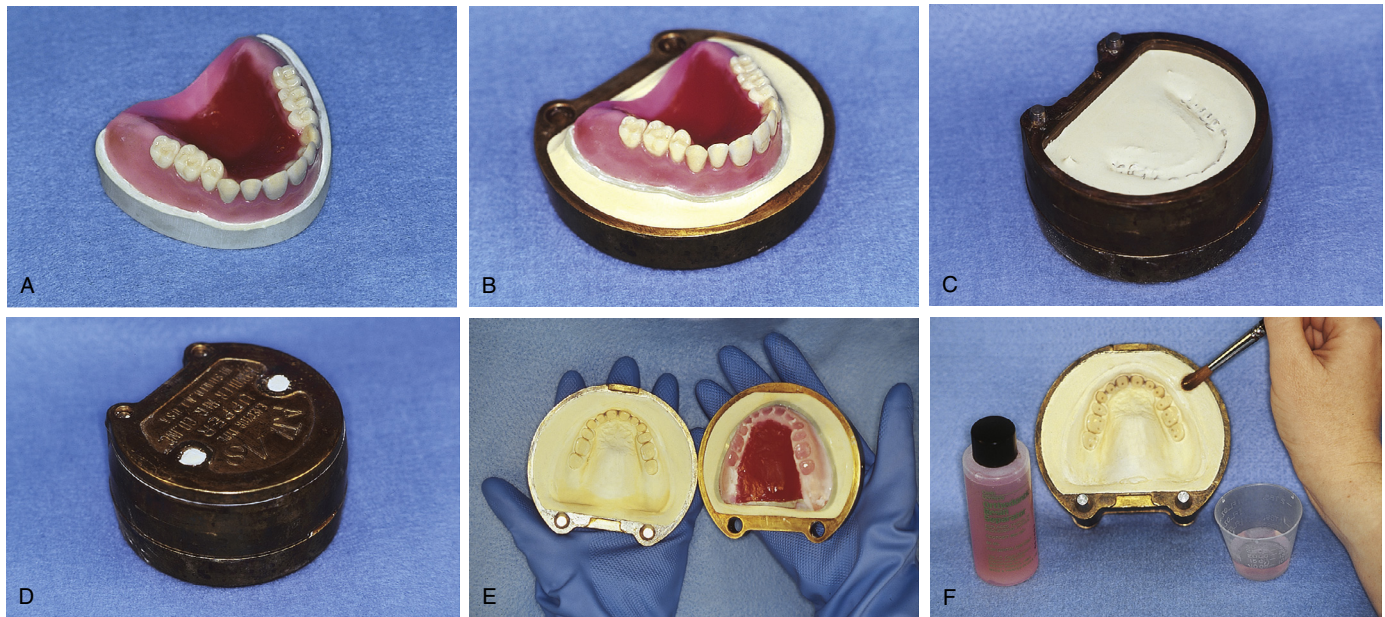
Not all denture base processing requires flasks. When light-activated resin or CAD-CAM processing is used, no flask is needed. In this chapter, we will discuss commonly available denture base materials and the properties and additional applications of denture base resins.



• **Figure 11-1** A representative heat-activated resin. The majority of heat-activated resins are supplied as powder-liquid systems. (Courtesy Lang Dental Mfg. Co., Inc., Wheeling, IL.)



• **Figure 11-2** Chemical basis for the formation of crosslinked poly(methyl methacrylate) (PMMA). Glycol dimethacrylate is incorporated into PMMA chains and may “bridge” or “interconnect” such chains.



• **Figure 11-3** Steps in mold preparation (compression molding technique). **A**, Completed tooth arrangement prepared for flasking process. **B**, Master cast embedded in properly contoured dental gypsum. **C**, Occlusal and incisal surfaces of the prosthetic teeth are exposed to facilitate subsequent denture recovery. **D**, Fully flanked complete maxillary denture. **E**, Separation of flask segments during wax-elimination process. **F**, Placement of alginate-based separating medium.

Heat-Activated Denture Base Resins

Heat-activated materials are used in the fabrication of nearly all denture bases. The use of heat-activated polymers involves the preparation of a gypsum mold for compression molding, preparation of denture base resin, and a thermal polymerization using a water bath or microwave oven.

Compression Molding Technique

As a rule, heat-activated denture base resins are shaped via compression molding. Therefore the compression molding technique is described in detail in the following subsections.

Preparation of the Mold

Before mold preparation, prosthetic teeth must be selected and arranged in a manner that will fulfill both esthetic and functional requirements. In turn, the completed tooth arrangement is sealed to the master gypsum cast.

At this stage, the master cast and completed tooth arrangement are removed from the dental articulator (*Figure 11-3, A*). The master cast is coated with a thin layer of separator to prevent adherence of dental gypsum to the master cast during the flasking process. The lower half of a denture flask is filled with freshly mixed gypsum, and the master cast is placed into this mixture. The gypsum is contoured to facilitate wax elimination, packing, and deflasking procedures (*Figure 11-3, B*). Upon reaching the initial set, the gypsum surfaces are coated with an appropriate separator.

The upper half of the selected denture flask is then positioned atop the lower half of the flask. A surface-tension-reducing agent is applied to exposed wax surfaces, and a second mix of dental gypsum is prepared. This increment of gypsum is poured into the denture flask. Care must be taken to ensure that the investing

material achieves intimate contact with all external surfaces of the mounted teeth. The investing gypsum is added until all surfaces of the tooth arrangement and denture base are completely covered. Incisal and occlusal surfaces are minimally exposed to facilitate subsequent deflasking (*Figure 11-3, C*). The gypsum is then permitted to set and is coated with a colorless separator.

At this point, an additional increment of gypsum is mixed, and the remainder of the flask is filled. The lid of the flask is gently seated, and the gypsum is allowed to harden (*Figure 11-3, D*).

After the gypsum has hardened, the record base and wax must be removed from the mold. To accomplish this task, the denture flask is immersed in boiling water for 4 minutes. The flask is then removed from the water, and the appropriate segments are separated. The record base and softened wax remain in the lower half of the denture flask, while the prosthetic teeth remain firmly embedded in the investing gypsum of the remaining segment (*Figure 11-3, E*). The record base and softened wax are carefully removed from the surface of the mold. Residual wax is removed from the mold cavity using wax solvent. The mold cavity is subsequently cleaned with a mild detergent solution and rinsed with boiling water.

CRITICAL QUESTIONS

What is the purpose of a separating medium that is used during denture base fabrication? What is the chemical basis for popular separating media?

Selection and Application of a Separating Medium

The next step in denture base fabrication involves the application of an appropriate separating medium onto the surfaces of the mold cavity. This medium prevents direct contact between the denture base resin and the mold surface. Failure to place an appropriate separating medium can lead to two major difficulties: (1) If water is permitted to diffuse into the denture base resin, the

moisture can affect the polymerization rate and the optical and physical properties of the resultant denture base. (2) If dissolved polymer or free monomer soaks into the mold surface, portions of the investing medium can fuse to the denture base, affecting the physical and esthetic properties of processed denture bases.

Currently, the most popular separating agents are water-soluble colloidal alginate solutions. When applied to gypsum surfaces, these solutions produce thin, relatively insoluble calcium alginate films. These films prevent direct contact of denture base resins and the surrounding dental gypsum.

A small amount of separator is dispensed into a disposable container. Then, a fine brush is used to apply the separating medium onto the exposed surfaces of a warm, clean gypsum mold (Figure 11-3, F). Separator should not contact the exposed portions of acrylic resin teeth because the separator interferes with chemical bonding between acrylic resin teeth and denture base resins. Subsequently, the mold sections are oriented to prevent “pooling” of separator and permitted to dry.

Preparation of Heat-Activated Denture Resin

As previously noted, most PMMA resin systems include powder and liquid components (Figure 11-1). The powder consists of spheres of PMMA, other copolymer, and a small amount of benzoyl peroxide, termed the *initiator*. Upon heating, the benzoyl peroxide generates free radicals, which are responsible for initiating polymerization. The liquid is predominantly methyl methacrylate monomer with small amounts of hydroquinone, as an *inhibitor* to prevent untimely polymerization of the liquid during storage. Inhibitors also retard the curing process and thereby increase working time.

Crosslinking agents, such as glycol dimethacrylate, may be added to the liquid. Glycol dimethacrylate is chemically and structurally similar to methyl methacrylate and can be incorporated into growing methyl methacrylate polymer chains (Figure 11-2). It is important to note that methyl methacrylate possesses one carbon-carbon double bond per molecule, and glycol dimethacrylate possesses two double bonds per molecule. As a result, an individual molecule of glycol dimethacrylate may serve as a “bridge” or “cross-member” linking two growing polymer chains. If sufficient glycol dimethacrylate is included in the mixture, numerous interconnections may be formed. These interconnections yield a net-like structure that provides resistance to deformation and solvent swelling that may be caused by exposure to ethanol in the diet. Crosslinking agents are incorporated into the liquid component at a concentration of 1% to 2% by volume.

CRITICAL QUESTIONS

Why do denture base resin systems contain polymer beads? How does the inclusion of polymer beads affect volumetric shrinkage?

Polymer-to-Monomer Ratio

A proper polymer-to-monomer ratio is important in the fabrication of well-fitting denture bases with desirable physical properties. Unfortunately, most discussions of the polymer-to-monomer ratio provide little practical information for dental personnel. Furthermore, these discussions do not address the relationships between molecular events and the gross handling characteristics of denture base resins.

As discussed in [Chapter 5, Composition and Function](#), on resin-based composites, the polymerization of denture base resins

results in shrinkage. Research indicates that the polymerization of methyl methacrylate monomers to form PMMA yields a 21% decrease in the volume of material. To minimize dimensional changes, resin manufacturers incorporate a significant fraction of polymer beads, like the fillers added in resin-based composites.

When the powder and liquid components are mixed in the proper proportions, a doughlike mass results. Commercial products generally exhibit a polymer-to-monomer ratio of approximately 3:1 by volume. This ratio provides sufficient monomer to thoroughly wet the polymer beads but does not contribute excess monomer that would produce increased polymerization shrinkage. Using a 3:1 ratio, the volumetric shrinkage can be limited to approximately 7% (about 2.3% linear shrinkage). Polymerization shrinkage is compensated by the initial setting expansion of the gypsum mold and swelling of the polymerized acrylic resin upon exposure to water in the denture flask and in clinical service. Consequently, the completed prosthesis displays little dimensional change.

CRITICAL QUESTIONS

What are the five physical stages through which properly mixed denture base resins pass? During which stage should compression molding be initiated?

Polymer-Monomer Interaction

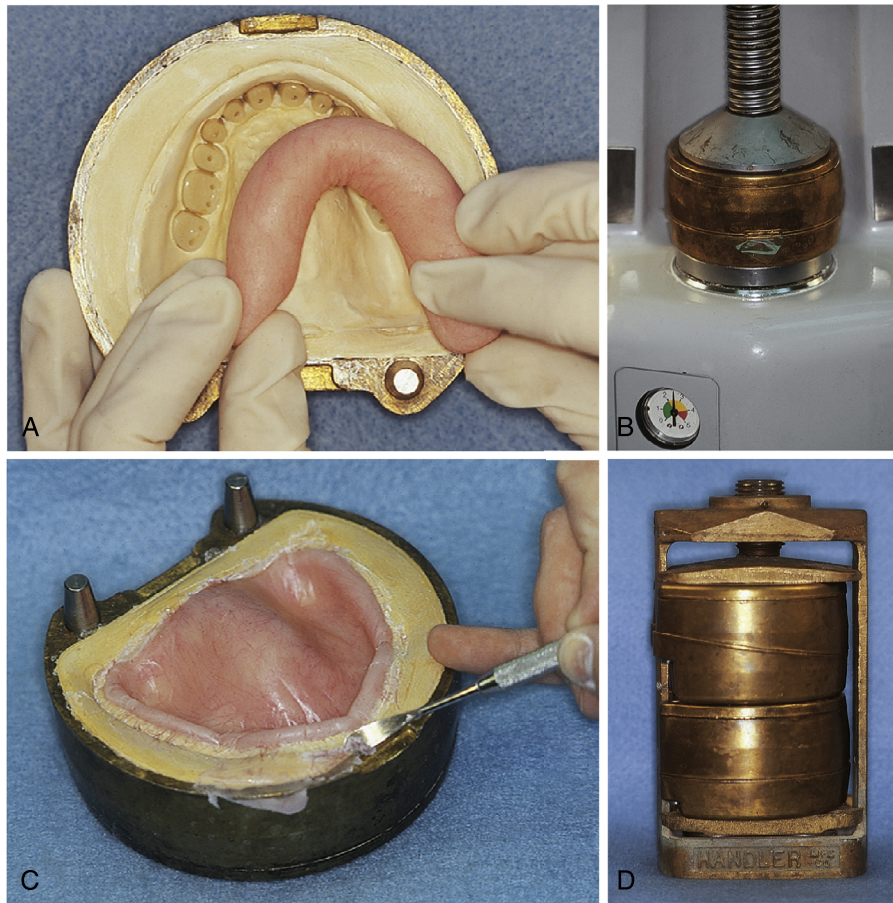
When monomer and polymer are mixed in the proper proportions, a workable mass is produced. Upon standing, without subjecting to heat for initiation of polymerization, the resultant mass passes through five distinct stages. These stages can be described as (1) *sandy*, (2) *stringy*, (3) *doughlike*, (4) *rubbery or elastic*, and (5) *stiff*.

During the sandy stage, little or no interaction occurs on a molecular level. Polymer beads remain unaltered, and the consistency of the mixture can be described as “coarse” or “grainy.” Later, the mixture enters a stringy stage when the monomer attacks the surfaces of individual polymer beads and is absorbed into the beads, causing swelling of the beads and dissolution of these non-crosslinked polymer chains into the liquid monomer. These polymer chains uncoil, thereby increasing the viscosity of the mix. This stage is characterized by “stringiness” or “stickiness” when the material is touched or drawn apart.

Subsequently, the mass enters a doughlike stage. On a molecular level, an increased number of polymer chains enter the solution. The mixture may be envisioned as polymeric strands within a volume of liquid monomer. (Visualize strands of cooked spaghetti in a pot containing water.) Clinically, the mass behaves as a pliable dough. It is no longer tacky and does not adhere to the surfaces of the mixing vessel or spatula. This is the ideal consistency for compression molding. As a result, the material should be introduced into the mold cavity during the latter phases of the doughlike stage.

Following the doughlike stage, the mixture enters a rubbery or elastic stage. This is because some monomer is dissipated by evaporation, and some penetrates further into remaining polymer beads. The mass rebounds when compressed or stretched. Because the mass no longer flows freely to assume the shape of its container, the rubbery acrylic is not moldable by conventional compression techniques.

Upon standing for an extended period, the mixture becomes stiff. This is the result of the evaporation of unreacted monomer. From a clinical standpoint, the mixture appears dry and is resistant to mechanical deformation.



• **Figure 11-4** Steps in resin packing (compression-molding technique). **A**, Properly mixed resin is bent into a horseshoe shape and placed into the mold cavity. **B**, The flask assembly is placed into a flask press, and pressure is applied. **C**, Excess material is carefully removed from the flask. **D**, The flask is transferred to a flask carrier, which maintains pressure on the assembly during processing.

Dough-Forming Time

The time required for the resin mixture to reach a doughlike stage is termed the *dough-forming time*. American National Standards Institute/American Dental Association (ANSI/ADA) Standard No. 139—Dental Base polymers: 2020 (ISO 20795-1:2013 Dentistry—Base polymers—Part 1: Denture base polymers) requires that this consistency be attained in less than 40 minutes from the start of the mixing process. In clinical use, the majority of denture base products reach a doughlike consistency in less than 10 minutes.

Working Time

Working time is defined as the time a denture base material remains in the doughlike stage. This period is critical to the compression molding process. ANSI/ADA Standard No. 139 requires the dough to remain moldable for at least 5 minutes.

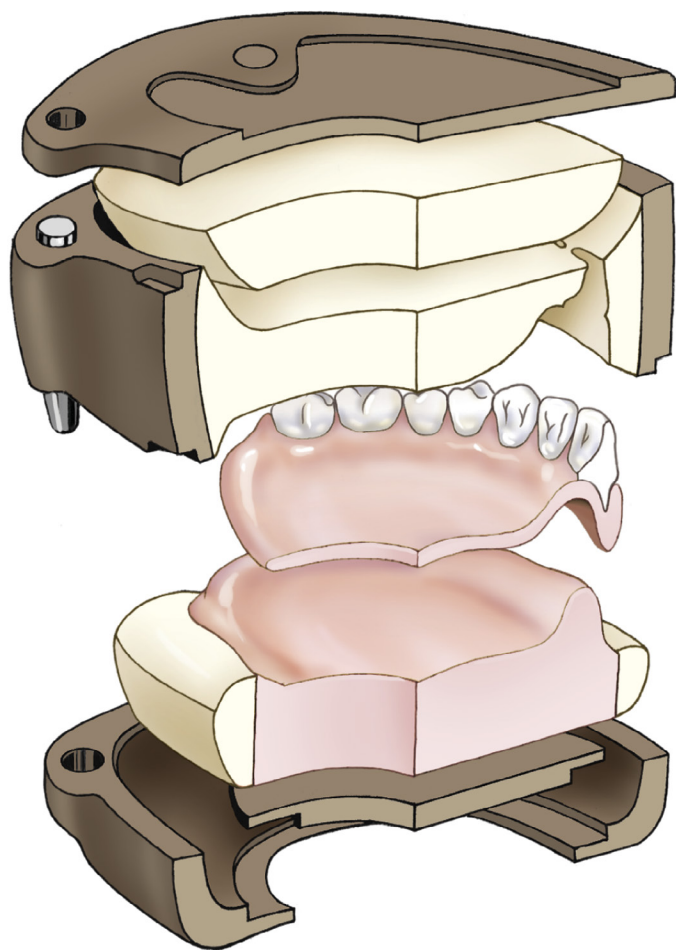
Ambient temperature affects the working time. Hence the working time of a denture resin can be extended via refrigeration. A significant drawback associated with this technique is that moisture may condense on the resin when it is exposed to ambient air. The presence of moisture may degrade the physical and esthetic properties of a processed resin. Moisture contamination can be avoided by storing the resin in an airtight container. Following removal from the refrigerator, the container should not be opened until it reaches room temperature.

Packing

The introduction of denture base resin into the mold cavity is termed *packing*. This process represents critical steps in denture base fabrication. While in a doughlike state, the resin is removed from its mixing container and rolled into a cylindrical form. Monomer is painted over the necks of the denture teeth to promote bonding to the denture base. Subsequently, the resin form is bent into a horseshoe shape and placed into the portion of the flask that houses the prosthetic teeth (Figure 11-4, A). A thin polyethylene packing sheet is placed over the master cast, and the flask is reassembled.

The flask assembly is placed into a press, and pressure is applied incrementally (Figure 11-4, B). Slow application of pressure permits the resin dough to flow uniformly throughout the mold space. The application of pressure is continued until the denture flask is fully closed. In turn, the flask is opened, and the polyethylene packing sheet is removed from the surface of the resin with a rapid, sustained tug.

Excess resin will be found on the relatively flat areas surrounding the mold cavity. This excess resin is called *flash*. Using a rounded instrument, the flash is carefully teased away from the body of resin that occupies the mold cavity (Figure 11-4, C). Care is taken not to chip the gypsum surfaces of the mold. Pieces of gypsum that have become dislodged must be removed so that they are not incorporated into the processed denture base.



• **Figure 11-5** A cross-sectional representation of the denture flask and its contents.

A fresh polyethylene packing sheet is placed between the major portions of the flask, and the flask assembly is once again placed in the press. Trial closures are repeated until minimal flash is observed.

At this stage, the mold is closed for the last time with no packing sheet interposed. The mold sections are aligned and placed in the flask press. Again, pressure is incrementally applied. Following definitive closure, the flask is transferred to a flask carrier (Figure 11-4, D), which maintains pressure on the flask assembly during denture base processing. A cross-sectional representation of the denture flask assembly is presented in Figure 11-5.

Injection Molding Technique

In addition to the compression molding techniques, denture bases can be fabricated via injection molding using specially designed flasks. One half of the flask is filled with freshly mixed gypsum, and the master cast is settled into this mixture. The gypsum is appropriately contoured and permitted to set. Subsequently, sprues or ingates are attached to the wax denture base to introduce resin during the injection-molding process (Figure 11-6, A). The remaining half of the flask is positioned, and the investment process is completed (Figure 11-6, B). Wax elimination is performed as previously described (Figure 11-6, C), and the flask is reassembled. Subsequently, the flask is placed into a carrier that maintains pressure on the assembly during resin introduction and processing.

Upon completion of the foregoing steps, resin is mixed and injected into the mold cavity (Figure 11-6, D). The flask is then

placed into a water bath for polymerization of the denture base resin if a heat-curing resin is used. Upon completion, the denture is recovered, adjusted, finished, and polished.

Currently, there is some debate regarding the comparative accuracy of denture bases fabricated by compression molding and those fabricated by injection molding. Available data and clinical information indicate that denture bases fabricated by injection molding can provide slightly improved clinical accuracy.

Polymerization Procedure

During denture base fabrication, heat is applied to the resin by immersing the denture flask and flask carrier in a water bath. The water is heated to a prescribed temperature and maintained at that temperature for a period suggested by the manufacturer.

Temperature Rise

The polymerization of denture base resins is exothermic, and the amount of heat evolved can affect the properties of processed denture bases. Representative temperature changes occurring in water, investing gypsum, and resin are presented in Figure 11-7. The temperature profile of the investing gypsum closely parallels the heating curve for the water. The temperature of the denture base resin lags somewhat during the initial stages of the heating process. This is caused by the fact that the resin occupies a position in the center of the mold, and therefore, heat penetration takes longer.

As the denture base resin rises slightly above 70 °C, the temperature of the resin begins to increase rapidly. In turn, the decomposition rate of benzoyl peroxide is significantly increased. This sequence of events leads to an increased rate of polymerization and an accompanying increase in the exothermic heat of reaction.

CRITICAL QUESTIONS

What causes porosity in denture bases? How can these defects be minimized?

Polymerization Cycle

Controlled heating processes are used to guide the polymerization of heat-activated denture bases. Such heating processes are termed *polymerization cycles* or *curing cycles*. The relationship between the heating rate and temperature rise within the denture base resin is illustrated in Figure 11-8. The polymerization cycle represented by curve C probably would yield porosity in thick portions of the denture because the temperature of the resin exceeds the boiling point of the monomer (100.8 °C). On the other hand, the polymerization cycle represented by curve A probably would result in the presence of residual monomer because the resin temperature does not reach the boiling temperature of the monomer. To minimize the likelihood of undesirable outcomes, carefully controlled heating cycles have been developed.

One technique involves processing the denture base resin in a constant-temperature water bath at 74 °C (165 °F) for 8 hours or longer, with no terminal boiling treatment. A second technique consists of processing in a 74 °C water bath for 8 hours, and then increasing the temperature to 100 °C for 1 hour. A third technique involves processing the resin at 74 °C for approximately 2 hours and increasing the temperature of the water bath to 100 °C and processing for 1 hour. All techniques are commonly used and equally effective.

Following completion of the chosen polymerization cycle, the denture flask should be permitted to cool to room temperature. Rapid cooling can result in distortion of the denture base because



• **Figure 11-6** Steps in mold preparation (injection molding technique). **A**, Placement of sprues for introduction of resin. **B**, Occlusal and incisal surfaces of the prosthetic teeth are exposed to facilitate denture recovery. **C**, Separation of flask segments during wax-elimination process. **D**, Injection of resin and placement of assembly into water bath.

of differences in the thermal contraction of resin and investing gypsum. To minimize potential difficulties, the flask should be removed from the water and bench-cooled for 30 minutes. Subsequently, the flask should be immersed in cool tap water for 15 minutes. The denture base may then be deflashed and prepared for delivery. To decrease the probability of unfavorable dimensional changes, the denture should be stored in water until the clinical fitting appointment.

Polymerization via Microwave Energy

PMMA resin may be polymerized using microwave energy because the methyl methacrylate molecule is asymmetrical and therefore “lossy.” This technique employs a specially formulated resin and a nonmetallic flask (Figure 11-9). A conventional 1100-watt, 24-GHz microwave oven is used to supply the thermal energy required for polymerization.

The major advantage of this technique is the speed with which polymerization may be accomplished. Despite the decreased processing time, overheating can occur in thick sections, causing the monomer to boil and yielding porosity. It should also be noted that although the polymerization time is reduced, the required technician time is unaffected. Available information indicates that the physical properties of microwave resins are comparable to those of conventional resins. Furthermore, the fit of denture bases polymerized using microwave energy is comparable to those processed via conventional compression molding techniques.

CAD-CAM Procedures in Denture Base Fabrication

Although the first CAM software program was developed by Dr. Patrick Hanratty in the 1950s, it was not until the 1990s that CAD-CAM technologies were used to generate complete dentures. The first English-language account of computer-aided technology in the fabrication of complete dentures was published by Maeda et al. in 1994. The authors employed stereolithography to generate complete dentures in a proof-of-concept effort. Beginning in 1995, Goodacre employed a series of procedures intended to facilitate the fabrication of complete dentures using subtractive techniques. In the ensuing years, Kawahata et al. and Kanazawa et al. used computer numerical control (CNC) milling to advance and refine previous efforts. CNC is an automated control of machining and 3-D printers by means of a computer. In 2012, Goodacre et al. published the first clinical account of CAD-CAM dentures milled from prepolymerized PMMA.

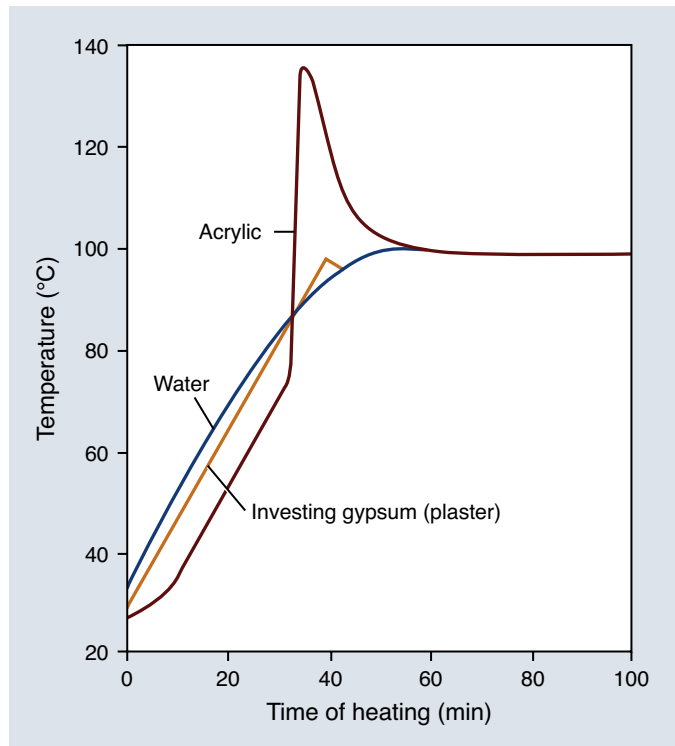
Advantages associated with CAD-CAM fabrication of complete dentures include enhanced material properties and improved dimensional stability of the resultant prostheses. PMMA “pucks” are fabricated at increased pressures and under strictly controlled thermal conditions. Consequently, these materials display decreased porosity, increased polymerization, and a diminished residual

monomer content. Moreover, the prepolymerized resins used in current subtractive processes are approximately 8% more dense than their conventionally processed counterparts. These factors are likely to yield enhanced clinical performance and decreased surface colonization by undesirable species such as *Candida albicans*.

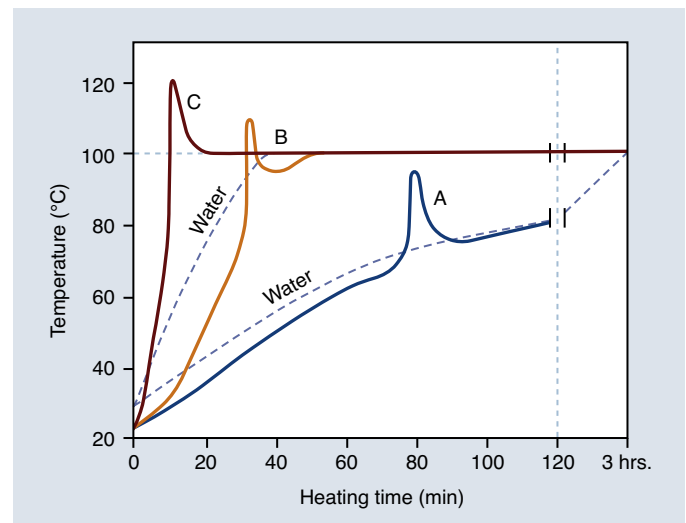
Machining of prepolymerized PMMA specimens also affects the clinical adaptation and the dimensional stability of completed denture bases. As previously noted, dentures fabricated via compression-molding techniques are subject to polymerization shrinkage during the fabrication process. In addition, compression-molded

prostheses are susceptible to distortion upon recovery from the mold. Corresponding changes are not observed in machined specimens because polymerization shrinkage and stress relaxation occur before the machining process. As a result, milled denture bases exhibit improved adaptation to the underlying ridges upon clinical placement and are less susceptible to distortion because relaxation has occurred prior to the machining process.

Currently, the most common CAD-CAM techniques for the fabrication of complete dentures employ milling technologies. Clinicians are responsible for accurately capturing the anatomical ridge forms, identifying critical landmarks (e.g., incisal edge position, facial midline, lip line, etc.), recording desired ridge/arch relationships, and determining appropriate tooth shades and forms. This information is transferred to the dental laboratory or manufacturer responsible for prosthesis fabrication. Design is accomplished in a virtual environment (CAD) and subsequently exported to a milling device for production (CAM).



• **Figure 11-7** Temperature-time heating curves for the water bath, investing plaster, and acrylic resin during the polymerization of a 25.4-mm cube of denture resin. (Modified from Tuckfield WJ, Worner HK, Guerin BD: Acrylic resins in dentistry. *Aust Dent J*, 47:119–121, 1943. Reproduced with permission from the Australian Dental Journal.)



• **Figure 11-8** Temperature changes in acrylic resin when subjected to various curing schedules. Curve A temperature rose to 100 °C in 3 hours, curve B temperature rose to 100 °C in 40 minutes, and curve C began at 100 °C. (Modified from Tuckfield WJ, Worner HK, Guerin BD: Acrylic resins in dentistry. *Aust Dent J*, 47:119–121, 1943. Reproduced with permission from the Australian Dental Journal.)



• **Figure 11-9** A representative microwave-activated resin system. **A**, Nonmetallic flask. **B**, Powder and liquid components of the resin. (Courtesy GC America, Inc., Alsip, IL.)

In the existing environment, dominant systems employ two-component manufacturing processes. The required denture base is manufactured as one component, and the corresponding teeth are manufactured as a separate yet continuous monolithic component. The denture base and tooth forms may be joined in a variety of ways, and the prosthesis is finished, polished, and prepared for clinical placement.

Critical Question

What are the benefits associated with the chemical-activated processes compared with heat-activated processes?

Chemical-Activated Denture Base Resins

The same initiator used in heat-activated denture base resin can also be activated by a tertiary amine, such as dimethyl-para-toluidine. The tertiary amine may be added to the liquid monomer. Upon mixing liquid and powder components, the tertiary amine causes decomposition of the benzoyl peroxide contained in the powder. As a result, free radicals are produced, and polymerization progresses in a manner similar to that described for heat-activated systems. Chemical activation does not require the application of thermal energy and can be completed at room temperature. For this reason, chemical-activated resins often are referred to as *cold-curing*, *self-curing*, or *autopolymerizing* resins.

Technical Considerations

The powder and liquid components are mixed according to the manufacturer's directions and permitted to attain a doughlike consistency. The working time for chemical-activated resins is shorter than that for heat-activated materials. Therefore special attention must be paid to the consistency of the material and rate of polymerization.

A lengthy initiation period is desirable because this provides adequate time for trial closures of the denture flask. One method for prolonging the initiation period is to decrease the temperature of the resin mass. This may be accomplished by refrigerating the liquid component and/or the mixing vessel before the mixing process. When the powder and liquid are mixed, the polymerization process is slowed, the resin mass remains in a doughy stage for an extended period, and the working time is prolonged.

Mold preparation and resin packing are accomplished in the same manner described for heat-activated resins. In cases of chemical-activated resins with minimal working times, it is doubtful that more than two trial closures can be made. Therefore extreme care must be taken to ensure that a proper amount of resin is employed, and a minimal number of trial closures are needed.

Processing Considerations

Following definitive closure of the denture flask, pressure must be maintained throughout the polymerization process. The time required for polymerization will vary with the material chosen.

Initial hardening of the resin generally will occur within 30 minutes, but polymerization continues for an extended period. To ensure sufficient polymerization, the flask should be held under pressure for a minimum of 3 hours.

The polymerization of chemical-activated resins is never as complete as the polymerization of heat-activated materials. Resins

polymerized via chemical activation generally display 3% to 5% free monomer, whereas heat-activated resins exhibit 0.2% to 0.5% free monomer. Therefore it is important that the polymerization of chemical-activated resins be as complete as possible. Failure to achieve a high degree of polymerization will predispose the denture base to dimensional instability and can lead to tissue irritation.

Heat-Activated Versus Chemical-Activated Denture Base

The residual monomer in chemical-activated denture base materials creates two difficulties. First, the residual monomer acts as a plasticizer, resulting in decreased transverse strength of the denture resin. Second, the residual monomer serves as a potential tissue irritant, thereby compromising the biocompatibility of the denture base.

From a physical standpoint, chemical-activated resins display slightly less shrinkage than their heat-activated counterparts. This imparts greater dimensional accuracy to chemical-activated resins.

The color stability of chemical-activated resins generally is inferior to the color stability of heat-activated resins. This property is related to the presence of tertiary amines within the chemical-activated resins. Such amines are susceptible to oxidation and accompanying color changes that affect the appearance of the resin. Discoloration of these resins can be minimized via the addition of stabilizing agents that prevent such oxidation.

Fluid-Resin Technique

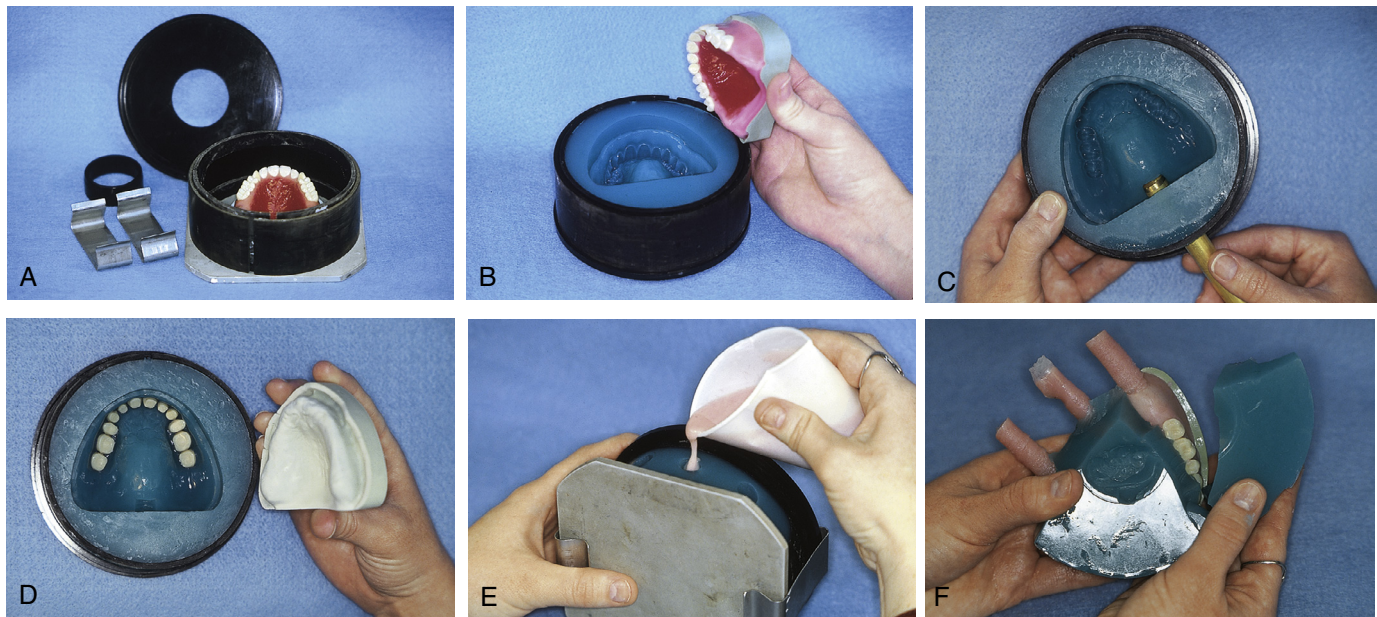
The fluid-resin technique employs a pourable, chemical-activated resin for the fabrication of denture bases. When mixed in the proper proportions, a low-viscosity resin is produced. This resin is poured into a mold cavity, subjected to increased atmospheric pressure, and allowed to polymerize at ambient temperature. Laboratory aspects of the fluid-resin technique are described in the following paragraphs.

Tooth arrangement is accomplished using accepted prosthodontic principles. The completed tooth arrangement is then sealed to the underlying master cast and placed in a specially designed flask ([Figure 11-10, A](#)). The flask is filled with a reversible hydrocolloid-based investment medium, and the assembly is cooled. Following gelation of the hydrocolloid, the master cast with the attached tooth arrangement is removed from the flask ([Figure 11-10, B](#)). At this stage, sprues and vents are cut from the external surface of the flask to the mold cavity ([Figure 11-10, C](#)).

Wax is eliminated from the cast using water. The prosthetic teeth are retrieved and carefully seated in their respective positions within the hydrocolloid investing medium. Subsequently, the master cast is returned to its position within the mold ([Figure 11-10, D](#)).

The resin is mixed according to the manufacturer's directions and poured into the mold via the sprue channels ([Figure 11-10, E](#)). The flask is then placed in a pressurized chamber (i.e., a pressure pot) at room temperature, and the resin is permitted to polymerize. According to available information, only 30 to 45 min are required for polymerization. Nevertheless, a longer period is recommended.

Following completion of the polymerization process, the denture is retrieved from the flask ([Figure 11-10, F](#)), and the sprues are removed. The denture/cast assembly is returned to the dental articulator for correction of processing changes. Subsequently, the



• **Figure 11-10** Steps in mold preparation (fluid-resin technique). **A**, Completed tooth arrangement positioned in a fluid-resin flask. **B**, Removal of tooth arrangement from reversible hydrocolloid investment. **C**, Preparation of sprues and vents for the introduction of resin. **D**, Repositioning of the prosthetic teeth and master cast. **E**, Introduction of pour-type resin. **F**, Recovery of the completed prosthesis.

denture base is finished and polished. At this stage, the denture should be stored in water to prevent dehydration and distortion.

Advantages claimed for the fluid-resin technique include (1) improved adaptation to underlying soft tissues; (2) decreased probability of damage to prosthetic teeth and denture bases during deflasking; (3) reduced material costs; and (4) simplification of the flasking, deflasking, and finishing procedures.

Potential disadvantages of the fluid-resin technique include (1) noticeable shifting of prosthetic teeth during processing, (2) air entrapment within the denture base material, (3) poor bonding between the denture base material and acrylic resin teeth, and (4) technique sensitivity.

In general, denture bases fabricated in this manner exhibit physical properties that are somewhat inferior to those of conventional heat-processed resins. Nonetheless, clinically acceptable dentures can be obtained using fluid resins.

Light-Activated Denture Base Resins

Light-activated denture base resins have been described as resin-based composites having matrices of urethane dimethacrylate (UDMA; [Figure 5-2](#)), microfine silica, and high-molecular-weight acrylic resin monomers. Acrylic resin beads are included as organic fillers. Blue light is the activator, and a photosensitizing agent such as camphorquinone serves as the initiator for polymerization. Single-component denture base resins are supplied in sheet and rope forms and are packed in lightproof pouches to prevent inadvertent polymerization ([Figure 11-11, A](#)). The most recent generation of light-activated denture base resins consists of three distinct components: (1) a base-forming resin, (2) a tooth-setting resin, and (3) a contouring resin.

A light-activated resin cannot be flaked in a conventional manner because opaque investing media prevent the penetration of light. Instead, a definitive prosthesis is sculpted on the master cast using the aforementioned resins ([Figure 11-11, B](#)). The

base-forming resin is first adapted to the master cast and cured in a high-intensity light chamber ([Figure 11-11, C](#)). Subsequently, the tooth-setting resin is used to attach the prosthetic teeth to the polymerized base and placed in the light chamber to polymerize the tooth-setting resin, thereby maintaining prosthetic teeth in the desired positions. Next, a contouring resin is used to generate the desired surface anatomy. The resultant prosthesis ([Figure 11-11, B](#)) is placed into the light chamber to complete the process of denture base fabrication. The denture is then removed from the cast, finished, and polished in a conventional manner.

Physical Properties of Denture Base Resins

The physical properties of denture base resins are critical to the fit and function of removable dental prostheses. Characteristics of interest include polymerization shrinkage, porosity, water sorption, solubility, processing stresses, and crazing. These characteristics are addressed in the following sections.

Polymerization Shrinkage

When methyl methacrylate monomer is polymerized to form PMMA, the density of the mass changes from 0.94 to 1.19 g/cm³. This change in density results in a volumetric shrinkage of 21%. When a conventional heat-activated resin is mixed at the suggested powder-to-liquid ratio, about one third of the mass is liquid monomer. The remainder of the mass is PMMA beads. Consequently, the volumetric shrinkage exhibited by the polymerized mass should be approximately 7%. This figure agrees with values observed in laboratory and clinical investigations.

Critical Question

Why is the relatively high volumetric shrinkage of a denture base resin not usually considered a significant clinical problem?



• **Figure 11-11** Steps in denture fabrication (light-activated denture base resins). **A**, Representative light-activated denture base resin. Sheet and rope forms are supplied in light-proof pouches to prevent inadvertent polymerization. **B**, Teeth are arranged, and the denture base is sculpted using light-activated resin. **C**, The denture base is placed into a light chamber and polymerized according to the manufacturer's recommendations. (Parts A and C courtesy Densply International, York, PA.)

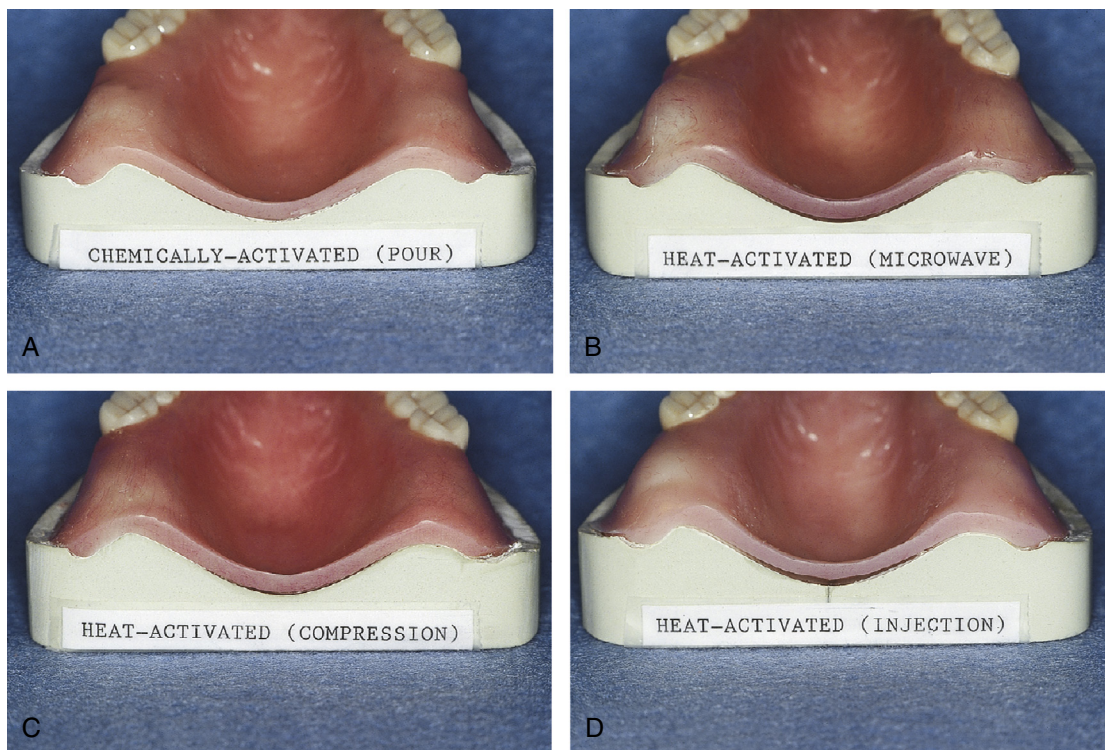
There are several possible reasons a material exhibiting high volumetric shrinkage can be used to produce clinically satisfactory denture bases. In addition to volumetric shrinkage, one also must consider the effects of linear shrinkage. Linear shrinkage exerts significant effects upon denture base adaptation and cuspal interdigitation. Based on a projected volumetric shrinkage of 7%, an acrylic resin denture base should exhibit a linear shrinkage of 2.3 %, approximately $\{1/3\}$ the value of the volumetric shrinkage. In reality, linear shrinkage within a denture base rarely exceeds 1% (Table 11-1).

Examination of the polymerization process indicates that thermal shrinkage of resin is primarily responsible for the linear changes observed in heat-activated systems. During the initial stages of the cooling process, the resin remains relatively soft. Consequently, the resin mass contracts at about the same rate as the surrounding gypsum.

TABLE 11-1 Polymerization Shrinkage of Maxillary Denture Bases

Material	Linear Shrinkage (%)
High-impact acrylic resin	0.12
Vinyl acrylic resin	0.33
Conventional acrylic resin	0.43
Pour-type acrylic resin	0.48
Rapid heat-cured acrylic resin	0.97

Data from Stafford GD, Bates JF, Huggett R, Handley RW: A review of the properties of some denture base polymers. *J Dent* 8:292, 1960.



• **Figure 11-12** Dimensional changes resulting from polymerization. **A**, Chemical-activated resin, pour technique. **B**, Microwave resin, compression molding. **C**, Conventional heat-activated resin, compression molding. **D**, Heat-activated resin, injection molding. (Demonstration and photographs courtesy Dr. Rodney Phoenix.)

As cooling proceeds, the soft resin approaches its glass-transition temperature, T_g , which is the thermal range in which the polymerized resin passes from a soft, rubbery state to a rigid, glassy state. Cooling the denture base resin beyond the glass-transition temperature yields a rigid mass. As might be expected, this rigid mass contracts at a rate different from that of surrounding dental gypsum. The shrinkage occurring below the glass-transition temperature is thermal in nature and varies according to the composition of the resin.

To illustrate the effect of thermal shrinkage, consider the following example. The glass-transition temperature for PMMA is approximately 105 °C. Room temperature is 20 °C. The generally accepted value for the linear coefficient of thermal expansion, α , for PMMA is 81 ppm/°C. Therefore, as the denture base resin cools from the glass-transition temperature to room temperature, the resin undergoes a linear shrinkage, which can be expressed as follows:

$$\text{Linear shrinkage} = \alpha \Delta T = (81 \times 10^{-6})(105 - 20) = 0.69\%$$

This value agrees with the linear shrinkages of 0.12% to 0.97% reported for various commercial denture base resins (see Table 11-1).

Complete dentures constructed using chemical-activated resins generally display better adaptation than those constructed using heat-activated resins. This phenomenon can be attributed to the negligible thermal shrinkage displayed by chemical-activated resins. Processing shrinkage has been measured as 0.26% for a

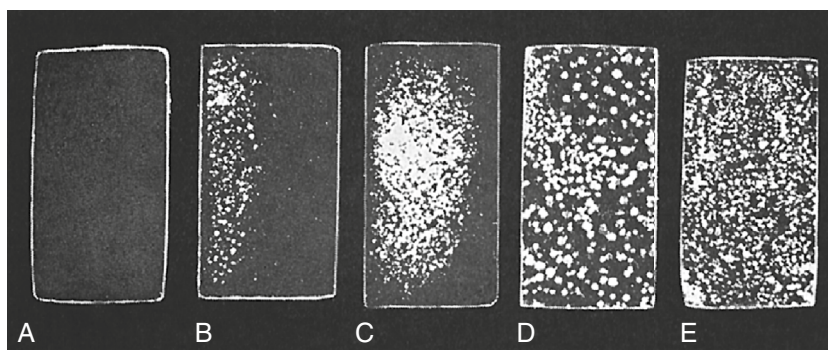
representative chemical-activated resin, compared with 0.53% for a representative heat-activated resin.

Given the preceding information regarding polymerization shrinkage and denture base adaptation, chemical-activated resins appear to provide significant advantages over heat-activated resins. However, there are several other factors that affect the dimensional characteristics of processed denture bases, including the type of investing medium, method of resin introduction, and temperature used to activate the polymerization process.

On completion of the polymerization process, individual denture bases and master casts are retrieved and returned to their respective dental articulator(s). Dimensional changes are assessed with respect to the proposed vertical dimension of occlusion.

Fluid-resin techniques used in conjunction with hydrocolloid investing media generally yield decreases in the vertical dimension. Conversely, dentures processed using heat-activated or chemical-activated resins in conjunction with compression molding techniques usually display increases in the overall vertical dimension. Minimal increases in the vertical dimension are considered desirable because they permit a return to the proposed occlusal vertical dimension via occlusal grinding procedures.

Dimensional changes occurring in denture bases fabricated from various resins are illustrated in Figure 11-12 as gaps at the posterior palatal border. Additional dimensional factors include the setting expansion of the gypsum product used to make the master cast and investing component and expansion from water sorption of the cured acrylic resin after polymerization is complete.



• **Figure 11-13** Heat-activated denture base resin exhibiting different types and degrees of porosity. **A**, Properly polymerized; no porosity. **B** and **C**, Rapid heating, relatively small subsurface voids. **D**, Insufficient mixing of monomer and polymer; large voids resulting from localized polymerization shrinkage. **E**, Insufficient pressure during polymerization; relatively large, irregular voids. (From Tuckfield WJ, Worner HK, Guerin BD: Acrylic resins in dentistry. *Aust Dent J*, 47:119–121, 1943.)

CRITICAL QUESTIONS

What are the causes of porosity when fluid-resin denture fabrication techniques are used? How can these difficulties be minimized?

Porosity

Porosity is noted to likely develop in thicker portions of a denture base. Such porosity results from the vaporization of unreacted monomers when the temperature of a resin reaches or exceeds the boiling points of these species. Nonetheless, this type of porosity may not occur equally throughout the affected resin segments.

Consider the specimens in [Figure 11-13](#), **A** (no porosity) and **B** and **C** (localized subsurface porosity). Specimens **B** and **C** were flaked in such a manner that the section displaying porosity was nearer to the center of the investment mass, whereas the nonporous section was nearer to the surface of the metal flask. As might be expected, the metal conducted heat away from the periphery, preventing the low-molecular-weight species from boiling and yielding porosity. In contrast, resin specimens surrounded by larger amounts of gypsum, a poor thermal conductor, were subjected to a significant exotherm that led to vaporization of low-molecular-weight species and noticeable porosity.

Porosity also may result from inadequate mixing of powder and liquid components. During polymerization, these regions shrink more than adjacent regions, and the localized shrinkage tends to produce voids ([Figure 11-13](#), **D**). The occurrence of such porosity can be minimized by ensuring the greatest possible homogeneity in the resin. Proper polymer-to-monomer ratios and well-controlled mixing procedures are essential. Because the material is more homogeneous in the doughlike stage, delay packing is wise until this consistency has been reached.

A third type of porosity can be caused by inadequate pressure or insufficient material in the mold during polymerization ([Figure 11-13](#), **E**). Voids resulting from these inadequacies are not spherical; they assume irregular shapes. These voids may be so abundant that the resultant resin appears significantly lighter and more opaque than the intended color.

A final type of porosity most often associated with fluid resins is air entrapment during mixing and pouring procedures. Careful mixing, spruing, and venting are essential in preventing such voids.

Water Sorption

PMMA absorbs small amounts of water when placed in an aqueous environment. As water molecules penetrate the PMMA mass, they occupy spaces between polymer chains. Consequently, the affected polymer chains are forced apart. The introduction of water molecules produces two important effects. First, the water causes a slight expansion of the polymerized mass. Second, water molecules interfere with the entanglement of polymer chains and thereby act as plasticizers. This permits the relaxation of stresses incurred during polymerization. As stresses are relieved, polymerized resins may undergo changes in shape. Fortunately, these changes are relatively minor and do not exert significant effects on the fit or function of the processed denture bases.

For each 1% increase in weight produced by water sorption, acrylic resin has been estimated to exhibit a linear expansion of 0.23%. Laboratory tests indicate that the linear expansion caused by water sorption is approximately equal to the thermal shrinkage encountered as a result of the polymerization process. Hence, these processes very nearly offset one another.

Because the presence of water adversely affects the physical and dimensional properties of denture base resins, diffusion coefficients also warrant consideration. The diffusion coefficient of water in representative heat-activated denture acrylic resin is $0.011 \times 10^{-6} \text{ cm}^2/\text{s}$ at 37°C . For a representative chemical-activated resin, the diffusion coefficient is $0.023 \times 10^{-6} \text{ cm}^2/\text{s}$. Because the diffusion coefficients of water in representative denture resins are relatively low, the time required for a denture base to reach saturation can be considerable. This is dependent on the thickness of the resin and the storage conditions. A typical heat-activated denture base may require a period of 17 days to become fully saturated with water.

The results of laboratory investigations indicate that there are very slight differences in the dimensions of heat-activated and chemical-activated denture bases following prolonged storage in water. Compression-molded heat-activated denture bases are slightly undersized when measured from second molar to second molar. Conversely, compression-molded chemical-activated denture bases are slightly oversized when measured in the same regions. The clinical significance of this difference is negligible.

ANSI/ADA Standard No. 139 identifies guidelines regarding the testing and acceptance of denture base resins. To test water sorption, a disk of material with specified dimensions is prepared

and dried to a constant weight. This weight is recorded as a baseline value. The disk is then soaked in 37 °C distilled water for 7 days. Again, the disk is weighed, and this value is compared with the baseline value. According to the specification, weight gain following immersion must not be greater than 32 $\mu\text{g}/\text{mm}^3$.

Solubility

Although denture base resins are soluble in a variety of liquids, they are virtually insoluble in the fluids commonly encountered in the oral cavity. ANSI/ADA Standard No. 139 prescribes a testing regimen for the measurement of resin solubility. This procedure is a continuation of the water-sorption test described in the preceding section. Following the required water immersion, the test disk is permitted to dry and is reweighed. This value is compared with the baseline value to determine weight loss. According to the standard, weight loss must not be greater than 8.0 $\mu\text{g}/\text{mm}^3$ for chemical-cured PMMA and 1.6 $\mu\text{g}/\text{mm}^3$ for heat-, light-, and microwave-activated PMMA.

CRITICAL QUESTIONS

What are the causes of processing stresses? What are the clinical implications of these stresses, if any?

Processing Stresses

Whenever a natural dimensional change is inhibited, the affected material sustains internal stresses. If stresses are relaxed, distortion of the material can occur. This principle has important ramifications in the fabrication of denture bases because stresses are commonly induced during processing.

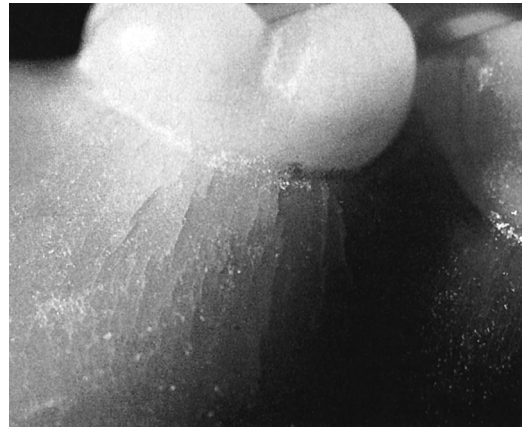
Consider the events that occur during denture base polymerization. A moderate amount of shrinkage occurs as individual monomers are linked to form polymer chains. During this process, friction between the mold walls and soft resin may inhibit normal shrinkage of these chains. In such instances, the polymer chains are stretched, and tensile stresses develop within the material.

Stresses also are produced as a result of thermal shrinkage. As a polymerized resin is cooled below this material's glass-transition temperature, the resin becomes relatively rigid. Further cooling results in thermal shrinkage. A denture base resin is encased in a rigid investing medium, such as dental gypsum, during this process. Because denture base resins and gypsum materials contract at different rates, a contraction differential is established. This disparity in contraction rates yields stresses within the resin. Additional factors that may contribute to processing stresses include improper mixing and handling of the resin and poorly controlled heating and cooling of the flask assembly.

Crazing

When dimensional changes alone cannot relieve internal stresses, hairline microcracks may develop as a means of dissipating energy and completing relaxation. The production of such flaws, or microcracks, is termed *crazing*.

Figure 11-14 shows crazing of denture base resin around porcelain teeth. Such damage may occur during cooling of the denture. When this occurs, the resin contracts more than the adjacent porcelain, and tensile stresses are established in the areas adjacent to the tooth. When these stresses exceed the



• **Figure 11-14** Crazing around porcelain teeth.

tensile strength of the resin, microcracking occurs, and craze lines result. Crazing in a transparent resin imparts a “hazy” or “foggy” appearance. In a tinted resin, crazing imparts a whitish appearance. Each craze line represents physical separation of the resin caused by tensile stresses. In addition to esthetic effects, these surface cracks predispose a denture resin to fracture. The widespread use of acrylic resin teeth of similar thermal contraction of the denture base resins has decreased the incidence of denture base crazing.

Crazing of denture base materials also may be induced by organic solvents. When PMMA is immersed in ethanol, the material swells as the ethanol diffuses into the PMMA mass. During this process, the solvent overcomes relatively weak van der Waals forces and produces narrow gaps in the denture base resin. Despite the creation of gaps, strong covalent bonds within the polymeric chains maintain the overall integrity of the material. Nevertheless, when the solvent evaporates, the gaps manifest as craze lines.

CRITICAL QUESTIONS

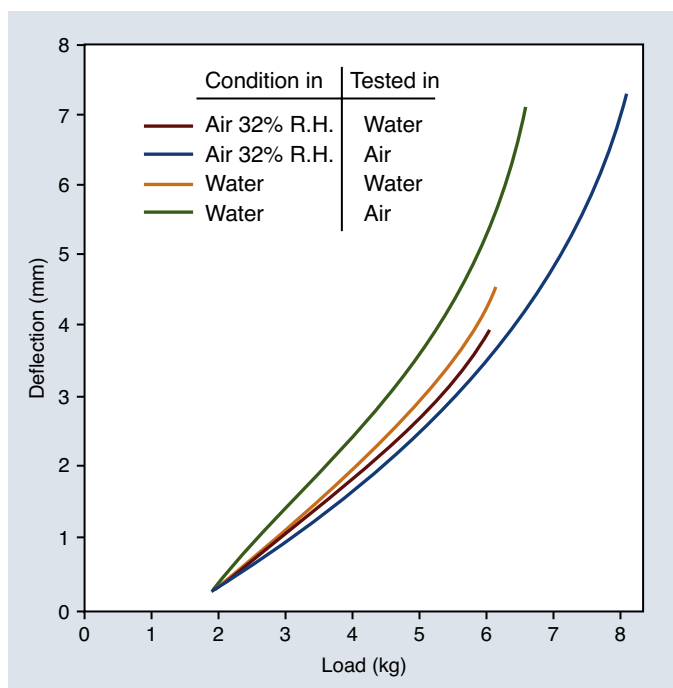
What variables reduce the strength of acrylic resin denture bases? What processing method is most likely to produce denture bases with decreased fracture resistance?

Strength

The strength of an individual denture base resin is dependent on many factors, including the composition of the resin, processing technique, and conditions presented by the oral environment.

To provide acceptable physical properties, denture base resins must meet or exceed the standards presented in ANSI/ADA Standard No. 139. A transverse test is used to evaluate the relationship between the applied load and resultant deflection in a resin specimen of prescribed dimensions. Representative deflection–load results are presented in Figure 11-15.

Inspection of Figure 11-15 reveals a curvature to each component of the deflection–load plot. Because no straight-line portion is evident, one may assume that plastic deformation occurs during the loading process. Some elastic deformation also occurs. From a clinical standpoint, this means that load application produces stresses within a resin and a change in the overall shape of the denture base. When the load is released, stresses within the resin are relaxed and the denture base begins to return to the denture's



• **Figure 11-15** Transverse deflection-load curve for a typical denture base resin, showing the influences of different conditioning procedures and testing environments. Before testing, all specimens were conditioned for 3 days as indicated. R.H., Relative humidity. (Data from Swaney AC, Paffenbarger GC, Caul HJ, et al.: American Dental Association Specification No. 12 (replaced by No. 139 in 2012) for denture base resin, second revision. *J Am Dent Assoc*, 46:54–66, 1953. Reprinted by permission of ADA Publishing, a Division of ADA Business Enterprises, Inc.)

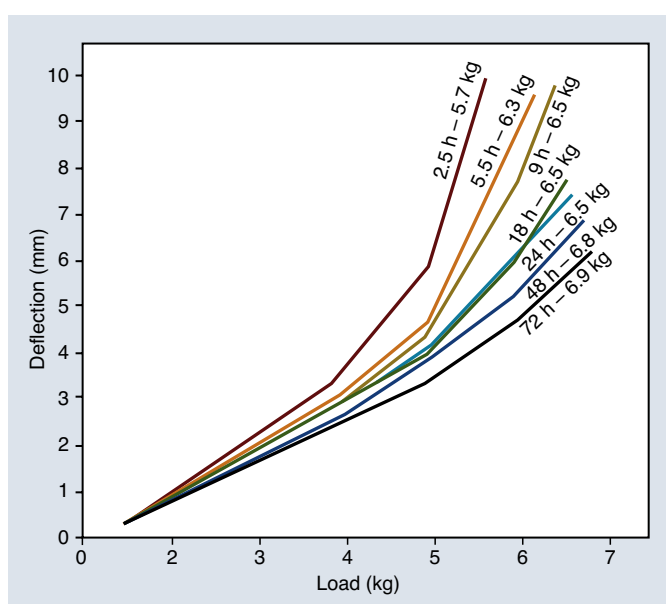
original shape. Nevertheless, plastic deformation prevents complete recovery.

Perhaps the most important determinant of resin strength is the degree of polymerization exhibited by the material. As the degree of polymerization increases, the strength of the resin also increases. Hence, the polymerization cycle employed with a heat-activated resin is important. Figure 11-16 reveals the effects that processing cycles exert on deflection-load properties. Note that a longer polymerization cycle appears to yield improved physical properties.

In comparison with heat-activated resins, the chemical-activated resins generally display lower degrees of polymerization. As a result, chemical-activated resins exhibit increased levels of residual monomer and decreased strength and stiffness. Despite these characteristics, heat- and chemical-activated resins display similar elastic moduli.

Impact Strength and Hardness

Charpy impact strengths for heat-activated denture resins commonly range from 0.98 to 1.27 joules, whereas those for chemical-activated resins are somewhat lower (0.78 joules). Impact strengths for high-impact resins such as Lucitone 199 may be twice those reported for conventional PMMA resins. Increased impact resistance is commonly imparted via the incorporation of rubbery hydrocarbon components such as butyl acrylate and polystyrene within the associated polymers. Clinicians should recognize that the preceding values are useful only for comparison of products because the energy absorbed by an individual specimen



• **Figure 11-16** Deflection-load curves for samples of poly(methyl methacrylate) polymerized for different periods at 71 °C (160 °F). Processing times and fracture loads are noted on individual curves. (Data from Harman IM: Effects of time and temperature on polymerization of a methacrylate resin denture base. *J Am Dent Assoc*, 38:188–203, 1949. Reprinted by permission of ADA Publishing, a Division of ADA Business Enterprises, Inc.)

is dependent on specimen size and geometry, the distance between specimen supports, and the presence or absence of notching.

Knoop hardness values for heat-activated resins may be as high as 20 KHN, whereas the associated values for chemically activated resins generally range from 16 to 18 KHN.

Creep

Acrylic denture resins display viscoelastic behavior. When a denture base resin is subjected to a sustained load, the material may exhibit deformation with both elastic (recoverable) and plastic (irrecoverable) components. If this load is not removed, additional plastic deformation can occur over time. This additional deformation is termed *creep*.

The rate at which this progressive deformation occurs is termed the *creep rate*. This rate can be elevated by increases in temperature, applied load, residual monomer, and/or the presence of plasticizers. Although creep rates for heat-activated and chemical-activated resins are very similar at low stresses, creep rates for chemical-activated resins increase more rapidly as stresses are raised.

Biological Properties of Denture Base Resins

Infection-Control Procedures

Care should be taken to prevent microbial and viral cross-contamination between patients and dental personnel, including personnel in the dental laboratory. New appliances should be disinfected before leaving the dental laboratory. Existing prostheses should be disinfected before entering the laboratory and following completion of laboratory procedures. All materials used for finishing and polishing should be handled according to established infection-control guidelines. Items such as rag wheels should be

autoclaved, and materials such as pumice should be used according to unit-dose recommendations.

Critical Question

Which components of denture resins are most likely to cause an allergic reaction?

Allergic Reactions

Possible toxic or allergic reactions to PMMA have long been postulated. Reactions can occur following contact with the polymers, residual monomers, benzoyl peroxide, hydroquinone inhibitor, pigments, or a reaction product between some component of the denture base and its environment. Despite the foregoing concerns, adverse reactions are more commonly related to uninterrupted denture wear.

Clinical experience indicates that true allergic reactions to acrylic resins seldom occur in the oral cavity. Irritation is slightly more common and is related to residual monomer. Irritation reactions are relatively rare because the residual monomer content of a properly processed denture is less than 1%. Furthermore, surface monomer is completely eliminated following storage in water for at least 17 hours.

Reactions to residual monomer should occur shortly after prosthesis delivery. However, the majority of patients reporting sore mouth resulting from denture wear have worn the offending prostheses for months or even years. Clinical evaluation of these cases indicates that tissue irritation is commonly related to continuous intraoral wear, fungal colonization, poor oral hygiene, trauma secondary to ill-fitting denture bases, and/or suboptimal denture occlusion.

Repeated or prolonged contact with monomer can also result in contact dermatitis. Personnel involved in the manipulation of denture resins most commonly experience this condition. Hence dental laboratory personnel should refrain from handling such materials with bare hands. The high concentration of monomer in freshly mixed resins may produce local irritation and serious sensitization of the fingers.

Finally, it should be noted that inhalation of monomer vapor may be detrimental. Therefore the use of monomer should be restricted to well-ventilated areas.

Toxicology

There is no evidence that commonly used dental resins produce systemic toxic effects in humans. As previously noted, the amount of residual monomer in processed PMMA is extremely low. To enter the circulatory system, residual monomer must pass through the oral mucosa and underlying tissues. These structures function as barriers that significantly diminish the volume of monomer reaching the bloodstream.

Residual monomer that does reach the bloodstream is rapidly hydrolyzed to methacrylic acid and excreted. It is estimated that the half-life of methyl methacrylate in circulating blood is 20 to 40 minutes.

Metal oxide (cadmium/selenium) red pigments were used for many years to color denture base resins. Although toxic in all concentrations, the pigments are locked within the denture base polymer network and used in very small concentrations. Nevertheless, most manufacturers have switched to organic pigment systems (e.g., Cromophthal Red BRN) to avoid such toxic effects.

Critical Question

What is the optimal technique for repairing a fractured acrylic denture base?

Additional Procedures Associated With Dentures

Denture Repair

Despite the favorable physical characteristics of denture base resins, denture bases sometimes fracture. In most instances, these fractures can be repaired using compatible resins. Repair resins may be light-, heat-, or chemical-activated.

To accurately accomplish the repair of a fractured prosthesis, the clinician must realign the denture components and stabilize them using an adherent wax or modeling plastic. When this has been accomplished, a repair cast is generated using dental gypsum. The denture is then removed from the cast, and the luting medium is eliminated. In turn, the fracture surfaces are trimmed to provide sufficient room for repair material and produce a survivable repair joint. The gypsum cast is coated with separating medium to prevent adherence of repair resin, and the denture base sections are repositioned and affixed to the cast.

At this point, a repair material is chosen. Chemical-activated resins are generally preferred over heat- and light-activated resins despite the fact that chemical-activated resins display lower transverse strength and color change. The principal advantage of chemical-activated resins is that they may be polymerized at room temperature. Heat- and light-activated repair materials must be placed in water baths and light chambers, respectively. Heat generated by water baths and light chambers often causes stress release and distortion of previously polymerized denture base segments.

The following sequence is employed to accomplish denture base repair using a chemical-activated resin. A small amount of monomer is painted onto the prepared surfaces of the denture base to promote bonding of the repair material. Increments of monomer and polymer are added to the repair area using a small sable-hair brush or suitable substitute. An excess of material is placed at the repair site to account for polymerization shrinkage. The assembly is placed in a pressure chamber under hot water and allowed to polymerize. The repair site is then shaped, finished, and polished using conventional techniques.

CRITICAL QUESTION

Under what conditions might resilient (soft) denture liners be used rather than rebasing an acrylic denture base?

Short-Term and Long-Term Resilient Soft Denture Liners

The purpose of a **resilient soft denture liner** is to absorb some of the energy produced by masticatory impact. Hence, a soft liner serves as a “shock absorber” between the occlusal surfaces of a denture and the underlying oral tissues. Liners also may provide added retention by entering anatomical undercuts if present. The most commonly used liners are plasticized acrylic resins. These resins may be heat-activated or chemical-activated resins and are based on familiar chemistries. Additional materials include silicone rubber, plasticized vinyl polymers and copolymers, polyphosphazene

fluoropolymers, and fluoroethylene and polyvinyl siloxane addition-cured silicones.

Compositions

All soft denture liners exhibit glass-transition temperatures that are lower than body temperature to allow sustained resilience. Most common materials used gain that property by incorporating plasticizer. Chairside resilient liners generally employ PMMA or poly(ethyl methacrylate) powder as principal structural components mixed with liquids containing 60% to 80% plasticizer. The plasticizer commonly is a large molecular species such as dibutyl phthalate or an alcohol. The distribution of large plasticizer molecules reduces the entanglement of polymer chains, thereby permitting individual chains to “slip” past one another, permitting changes in the shape of the soft liner and providing a cushioning effect for the underlying tissues. It is important to note that the liquids used in such applications do not contain acrylic monomers. Consequently, the resultant liners are considered **short-term soft liners**, or **tissue conditioners**.

Although plasticizers impart flexibility, they also present certain difficulties. Plasticizers are not bound within the resin mass. Therefore they may be “leached out.” As this occurs, resilient liners may become progressively more rigid. Hence, the use of liners that are less prone to leaching is advantageous.

In recent years, the phthalate esters have attracted attention because they mimic estrogenic hormones in the body after they migrate from the liner. Alternatives are now in use, including trimellitates, aliphatic dibasic esters, phosphates, benzoates, citrate esters, polymeric plasticizers, sulfonic acid, chloroparaffins, and sorbitol.

As PMMA is replaced by higher-molecular-weight methacrylates (e.g., ethyl, n-propyl, and n-butyl), the T_g becomes progressively lower (**Chapter 2, Thermal Properties**). As a result, less plasticizer is required, and the effects of leaching can be minimized.

Perhaps the most successful materials for soft liner applications have been the silicone rubbers. These materials are not dependent on leachable plasticizers, and they retain their elastic properties for prolonged periods. Unfortunately, silicone rubbers do not absorb shock and may lose adhesion to underlying denture bases over time. They are prone to colonization by fungi, which grow in the pores in the material and are difficult to remove.

Silicone rubbers may be chemical-activated or heat-activated silicones. Chemical-activated silicones are supplied as two-component systems that polymerize via condensation reactions.

Processing Resilient Soft Denture Liners

To reline a denture, the denture base is relieved to permit an acceptable thickness of the chosen material. A special adhesive is applied to the surface of the denture base to facilitate bonding. The resilient material is mixed, applied to the denture base via compression molding, and permitted to polymerize. In turn, the denture is recovered, finished, and polished. As with all resilient liners, the use of rotary instruments that rotate from the liner toward the denture base to prevent the initiation of peeling is important.

Heat-activated silicones are one-component systems supplied as pastes or gels. These materials are applied and contoured using compression molding techniques. Heat-activated silicones may be applied to polymerized resin bases, or they may be polymerized in conjunction with freshly mixed resins.

To promote adhesion between silicone resilient liners and rigid denture base materials, rubber-PMMA cements often are used.

These cements serve as chemical intermediates that bond to both soft liners and denture resins. The strongest bonds occur against fresh acrylic.

At least one silicone liner does not require an adhesive when it is cured together with an acrylic denture base material. This material actually is a silicone copolymer that contains components capable of bonding with acrylic resins.

Care of Denture Resilient Soft Liners

All soft liners display certain shortcomings. For instance, silicone liners are poorly adherent to denture base resins. Many resilient soft liners bond well to denture bases but become progressively more rigid as plasticizers are lost to the oral environment. Hardening rates for these liners are associated with the initial plasticizer content. As the plasticizer content is increased, the probability of plasticizer loss is increased. Hence, materials with a high initial plasticizer content tend to harden rather rapidly.

Resilient liners also exert significant effects on associated denture bases. As the thickness of a soft liner is increased, the thickness of the accompanying denture base must be decreased, and this results in decreased denture base strength. This may result in fracture of the denture base during clinical service.

Perhaps the greatest difficulty associated with silicone long- and short-term resilient liners is that these materials cannot be cleaned effectively. As a result, patients often report disagreeable tastes and odors related to these materials. The liners themselves do not support mycotic growth, but such growth is supported by debris that accumulates in the pores of these materials. The most common fungal growth associated with soft liners is *C. albicans*.

Several cleaning regimens have been used in conjunction with resilient liners. These regimens have met with limited success. Both oxygenating and hypochlorite-type denture cleansers have been employed. Unfortunately, these agents can cause significant damage to resilient soft liners, particularly the silicone materials.

Mechanical cleaning of resilient liners also may lead to damage, but such debridement often is necessary. If mechanical cleaning is undertaken, a soft brush should be used in conjunction with a mild detergent solution or nonabrasive dentifrice.

In attempts to address potential problems, antimycotic agents have been incorporated into soft liners. Although this approach is promising, the limited duration of antimycotic activity is far from ideal. Therefore additional research is warranted.

In 1989, a **long-term soft resilient liner** was introduced that uses a polyphosphazene fluoroelastomer with a $-(P=N)-$ backbone and interpenetrating di- and tri-functional crosslinking acrylics, pigment, and $BaSO_4$ filler. The liner is compression-molded against fresh acrylic and heat-cured conventionally. The material has no plasticizers, absorbs chewing forces because of its high energy damping, resists fungal overgrowth, is radiopaque, and is machinable.

CRITICAL QUESTION

Why are denture relining materials considered temporary-use products?

Relining Resin Denture Bases

Because alveolar ridge contours change with time, it is sometimes necessary to alter the tissue surfaces of prostheses to ensure proper fit. In some instances, this can be achieved by selective grinding procedures. In other instances, tissue surfaces must be replaced by **relining** or **rebasing** existing dentures.

Relining involves replacement of the tissue surface of an existing denture, whereas rebasing involves replacement of the entire denture base except for the denture teeth. In both instances, an impression of the soft tissues is made using the existing denture as an impression tray. A gypsum cast is generated in the impression, and the resultant assembly is invested in a denture flask. Subsequently, the flask is opened and prepared for the introduction of resin.

At this stage, the impression material is removed from the denture. The tissue surface is cleaned to enhance bonding between the existing denture base and the reline material. Next, an appropriate resin is introduced and shaped using a compression-molding technique.

For relining, a low polymerization temperature is desirable to minimize distortion of the remaining denture base. Hence, a chemical-activated resin is usually chosen. The selected material is mixed according to the manufacturer's recommendations, placed into the mold, compressed, and permitted to polymerize. Finally, the denture is recovered, finished, and polished.

If a chemical-activated resin is selected for relining the existing denture, a specialized mounting assembly may be used in lieu of flasking. This assembly maintains the correct vertical and horizontal relationships between the cast and the denture, while eliminating the need to encase the remaining denture base in dental gypsum. This facilitates recovery of the denture at the end of the relining process.

Relining can also be accomplished using resins that are activated by heat, light, or microwave energy. In all of these instances, significant heat can be generated, and distortion of the existing denture base will be more likely.

Similar materials are marketed for home use. Unfortunately, the majority of patients do not possess adequate knowledge to manipulate these materials correctly; therefore the use of such products can result in damage to the oral tissues and should be discouraged.

Rebasing Resin Dentures

The steps required in denture rebasing are similar to those described for relining. An accurate impression of the soft tissues is made using the existing denture as a custom tray. Subsequently, a gypsum cast is fabricated in the impression. The cast and denture are mounted in a device designed to maintain the correct vertical and horizontal relationships between the gypsum cast and surfaces of the prosthetic teeth. The resultant assembly provides indices for the occlusal surfaces of the prosthetic teeth. After these indices have been established, the denture is removed, and the teeth are separated from the existing denture base. The teeth are repositioned in their respective indices and held in their original relationships to the cast while they are waxed to a new baseplate.

At this point, the denture base is waxed to the desired form. The completed tooth arrangement is sealed to the cast, and the assembly is invested as previously described. Following elimination of the wax and removal of the baseplate, freshly mixed denture base resin is introduced into the mold cavity. Subsequently, the denture base is processed, recovered, finished, and polished. The completed prosthesis consists of a new denture base in conjunction with teeth from the patient's previous denture.

Resin Impression Trays and Tray Materials

Resin trays are commonly used in dental impression procedures. Unlike stock trays, resin impression trays are fabricated to fit the

arches of individual patients. Therefore resin impression trays are commonly called "custom trays."

The majority of custom trays are fabricated using light-activated and chemical-activated resin systems. Each system has advantages and disadvantages. Light-activated materials eliminate methyl methacrylate exposure but are more expensive and require high-intensity light units for polymerization. Chemical-activated resins are less expensive but have been associated with contact dermatitis, particularly in laboratory personnel.

The steps in custom tray fabrication may be described as follows: A preliminary impression is made using a stock tray and an appropriate impression material. In turn, a gypsum cast is generated. A suitable spacer (e.g., putty silicone [avoid wax]) is placed on the gypsum cast to provide the desired relief. Subsequently, a separating medium is applied to the surface of the cast. At this stage, fabrication techniques for light-activated materials and chemical-activated materials become divergent.

Light-activated resins are supplied in rope, sheet, and gel forms. Sheet forms are preferred for custom tray fabrication because of their favorable handling characteristics. Individual sheets are pliable and can be adapted to the associated casts and spacers with relative ease. A handle is added to facilitate removal of the tray from the mouth, the entire assembly is placed in a light chamber, and the resin is polymerized.

Chemical-activated resins typically are PMMA and are supplied as powder-liquid systems. The components are mixed to form a doughlike mass. The dough is then rolled into a sheet approximately 2 mm thick, adapted to the diagnostic cast with a handle as described previously, and allowed to polymerize.

Upon completion of the fabrication process, both light-activated and chemical-activated custom trays are removed from the associated casts and mechanically trimmed. The peripheries are rounded to make sure that patients will not be harmed by sharp or irregular edges. At this point, trays are evaluated intraorally and refined as necessary.

Denture Cleansers

Patients use a wide variety of agents for cleaning artificial dentures. These include dentifrices, proprietary denture cleansers, mild detergents, household cleansers, bleaches, and vinegar.

The most common commercial products are based on immersion techniques. These cleansers are marketed in powder and tablet forms containing alkaline compounds, detergents, sodium perborate, and flavoring agents. When dissolved in water, sodium perborate decomposes to form an alkaline peroxide solution. This solution subsequently releases oxygen, which loosens debris via mechanical means.

Household bleaches (hypochlorites) are also used in denture cleaning applications. Dilute bleach solutions can be used to remove certain types of stains. Unfortunately, prolonged use of bleach-containing solutions can remove color from denture bases, denture liners, and prosthetic teeth.

Bleaches and bleach solutions should not be used for cleaning metal prostheses such as removable partial denture frameworks. These solutions produce significant darkening of base metals and may irreparably damage the affected prostheses.

The use of brushes and abrasive cleansers can produce a range of effects on resin surfaces. Toothbrushes alone produce minimal wear of resin surfaces. Toothbrushes in conjunction with most commercial dentifrices, mild detergents, and soaps also appear to be relatively nondestructive. Conversely, household cleansers,

such as kitchen and bathroom abrasives, are contraindicated. Prolonged use of such cleansers may cause noticeable wear of resin surfaces and adversely affect the function and esthetics of these prostheses. Therefore patients should be educated regarding the care and cleaning of dental prostheses.

CRITICAL QUESTIONS

What precautions should be taken when using porcelain teeth in a denture? What are the clinically relevant differences between porcelain teeth and acrylic resin teeth?

Resin Teeth for Prosthetic Applications

The majority of preformed artificial teeth sold in the United States are made of acrylic or vinyl-acrylic resins. As might be expected, the methacrylate chemistries used in the fabrication of prosthetic teeth are similar to those used in denture base construction. The degree of crosslinking at the occlusal and incisal surfaces of prosthetic teeth is much greater than that exhibited by polymerized denture base materials. The increased crosslinking of prosthetic teeth in conjunction with the addition of inorganic filler increases wear resistance and improves clinical properties.

Cervical portions of prosthetic teeth often exhibit reduced crosslinking to facilitate chemical bonding with denture base resins. Additional retention may be achieved by removing the glossy “ridge-lap” surfaces of resin teeth and preparing mechanical undercuts.

Chemical bonding between resin teeth and heat-activated denture base materials has proven extremely effective. Nevertheless, bond failures can occur if ridge-lap surfaces are contaminated by residual wax or misplaced separating media. To optimize bonding, gypsum molds must be flushed with hot water, and the exposed cervical portions of prosthetic teeth must be thoroughly cleaned with mild detergent solutions. Separating media must be applied to gypsum mold surfaces but must not extend onto the exposed surfaces of resin teeth. As a final measure, ridge-lap surfaces should be wetted with monomer immediately before resin introduction.

To enhance the wear resistance of prosthetic dentitions, manufacturers have introduced “hybrid” teeth exhibiting multilayer construction. These teeth include both resin composites and PMMA components. Resin composites are found primarily on occlusal and incisal surfaces of the prosthetic teeth and are intended to provide improved wear resistance. Unfortunately, chemical bonding between resin composites and heat-activated denture base materials is inferior to that which occurs between resin teeth and such denture base materials. To address this shortcoming, manufacturers have incorporated PMMA at the ridge-lap and lingual surfaces of hybrid teeth. The presence of PMMA on these surfaces facilitates predictable bonding with heat-activated PMMA resins. Nevertheless, operators must be certain not to eliminate the PMMA surfaces during the tooth-arrangement process.

Despite the current emphasis on resin teeth, prosthetic teeth also may be fabricated using vacuum- or pressure-fired feldspathic porcelains. Hence a comparison of resin and porcelain teeth is warranted.

Resin teeth display greater impact resistance and ductility than porcelain teeth. As a result, resin teeth are less likely to chip or fracture on impact, such as when a denture is dropped. Furthermore, resin teeth are easier to adjust, and they display greater resistance to thermal shock. In contrast, porcelain teeth display improved dimensional stability and increased wear resistance.

Unfortunately, porcelain teeth often cause significant wear of opposing enamel, metal, and resin tooth surfaces, especially when contacting surfaces have been roughened. As a result, porcelain teeth should not oppose such surfaces, and if they are used, they should be polished periodically to reduce abrasive damage.

It should be noted that resin teeth are capable of chemical bonding with commonly used denture base resins. Porcelain teeth do not form chemical bonds with denture base resins and must be retained by bonded pins, mechanical undercuts, and/or silanization. As an additional consideration, leakage at the tooth–denture base junction can be seen as a dark line when food and microbes penetrate the interface.

CRITICAL QUESTION

What are the benefits and drawbacks of the materials used in the construction of maxillofacial prostheses?

Materials for Maxillofacial Prosthetics

For centuries, prostheses have been used to mask maxillofacial defects. The ancient Egyptians and Chinese used waxes and resins to reconstruct missing portions of the craniofacial complex. In the 16th century, the French surgeon Ambroise Paré described a variety of simple prostheses used for the cosmetic and functional replacement of maxillofacial structures. During the ensuing years, restorative techniques and materials were improved and refined. Casualties in World Wars I and II established an increased need for maxillofacial prosthetics, and the dental profession assumed a major role in maxillofacial reconstruction and rehabilitation processes.

Despite improvements in surgical and restorative techniques, the materials used in maxillofacial prosthetics are far from ideal. An ideal material should be inexpensive, biocompatible, strong, and stable. In addition, the material should be skinlike in color and texture. Maxillofacial materials should exhibit tear resistance when used in thin films, should exhibit compatibility with skin adhesives, and should be able to withstand moderate thermal and chemical challenges. Currently, no material fulfills all of these requirements. A brief summary of maxillofacial materials is included in the following paragraphs.

Latexes

Latexes are soft, inexpensive materials that can be used to create lifelike prostheses. Unfortunately, these materials are weak, degenerate rapidly, and exhibit color instability. Therefore latexes are rarely used in the fabrication of long-term maxillofacial prostheses.

One synthetic latex is a terpolymer of butyl acrylate, methyl methacrylate, and methyl methacrylamide. Superior to natural latex, this material is nearly transparent. Colorants are sprayed onto the reverse or tissue side of the prosthesis, thereby providing enhanced translucency and improved blending. Despite these advantages, the associated technical processes are lengthy, and the resultant prostheses last only a few months. Therefore synthetic latexes have limited applications.

Vinyl Plastisols

Plasticized vinyl resins are sometimes used in maxillofacial applications. Plastisols are thick liquids composed of small vinyl particles dispersed in a plasticizer. Colorants are added to these materials

to match individual skin tones. Subsequently, vinyl plastisols are heated to impart desired physical characteristics. Unfortunately, vinyl plastisols harden with age as a result of plasticizer migration. Ultraviolet light also has an adverse effect on these materials. For these reasons, the usefulness of vinyl plastisols is limited.

Silicone Rubbers

Silicones were introduced in the mid-1940s and have been used in maxillofacial applications since the 1950s. Both heat-curing and room-temperature-curing silicones are in use today, and both exhibit advantages and disadvantages.

Room-temperature-curing silicones are supplied as single-component materials that cure by the evaporation of acetic acid. They are intrinsically colored by the addition of dyed rayon fibers, dry earth pigments, and/or oil-based pigments. Prostheses are polymerized by bulk packing in two- or three-part gypsum molds, although more durable molds have been made from epoxy resins or metals.

Heat-curing silicones are supplied as semisolid or puttylike materials and are intrinsically colored via the addition of suitable pigments. Following introduction into an appropriately constructed mold, the resultant assembly is exposed to a 30-minute heat application cycle at 180 °C. Heat-curing silicones display better strength and color stability than room-temperature-curing silicones. Nevertheless, all silicones are susceptible to fungal growth and fraying at fine margins, so a process of bonding to a sheet of polyurethane on the tissue surface has been developed. This process not only enhances prosthesis longevity but also improves the effectiveness of skin adhesives.

The major disadvantage of heat-curing silicones is the requirement for a milling machine and a press. Furthermore, a metal mold normally is used, and fabrication of the mold is a lengthy

procedure. A gypsum mold may be housed within a brass denture flask, but this increases the risk of damage to the silicone material during deflasking.

Polyurethane Polymers

Polyurethane also can be used in maxillofacial prosthetics. Fabrication of a polyurethane prosthesis requires accurate proportioning of three components. The material is placed in a gypsum or metal mold and allowed to polymerize at room temperature. Although a polyurethane prosthesis has a natural feel and appearance, it is susceptible to rapid deterioration, color change from the diet, and fungal growth.

Chlorinated Polyethylene

In an effort to overcome the deficiencies of the latex, vinyl plastisol, silicone, and polyurethane materials, a thermoplastic elastomer based on chlorinated polyethylene (CPE) was investigated in the 1970s and 1980s. With further development, CPE was shown to provide higher edge strength, permanent elasticity, and minimal fungal growth. In a recent randomized, controlled clinical trial, it was found that the material was equally preferred by patients who had never worn facial prostheses before, but patients who had worn silicone rubber prostheses in the past favored that material in the trial. Methods of layering the prosthetic material in the molds to develop color at depth and laminating surface coloration were also reported, which may be useful in future maxillofacial prosthetics applications.

Additional information may be found in a review by Lemon et al. (2005), which presents current concepts regarding facial prosthetic rehabilitation of patients with head and neck cancer and facial prosthetic biomaterials.

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Full Selected Readings for this chapter can be found on www.expertconsult.com.

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12

Dental Implants

OUTLINE

History of Dental Implants
 Classification of Implants
 Implant Components
 Implant Surgical Placement
 Evaluation of Clinical Success

Implant Biomaterials
 Selecting an Implant System
 Biocompatibility of Implants
 Biomechanics
 Summary

KEY TERMS

Alloplastic Related to implantation of an inert foreign body.
Ankylosis A condition of joint or tooth immobility resulting from oral pathology, surgery, or direct contact with bone.
Bioacceptance The ability to be tolerated in a biological environment in spite of adverse effects.
Bioactive Capable of promoting the formation of hydroxyapatite and bonding to bone.
Endosteal implant A device placed into the alveolar and/or basal bone of the mandible or maxilla that transects only one cortical plate.
Epithelial implant A device placed within the oral mucosa.
Implantation The process of grafting or inserting a material such as an inert foreign body (alloplast) or tissue within the body.

Micromotion The displacement of the implant root relative to the bone when the implant is loaded as a result of lack of friction or bone integration.
Osseointegration The process by which living bony tissue forms to within 100 Å of the implant surface without any intervening fibrous connective tissue.
Osteoinductive Ability to promote bone formation through a mechanism that induces the differentiation of osteoblasts.
Replantation Reinsertion of a tooth back into its jaw socket soon after intentional extraction or accidental removal.
Subperiosteal implant A dental device that is placed beneath the periosteum and overlies cortical bone.
Transosteal implant A device that penetrates both cortical plates and the thickness of alveolar bone.

The restoration and replacement of missing teeth are important aspects of modern dentistry. As teeth are lost to decay, disease, and trauma, there is a demand for improvement of esthetics and restoration of function.

Conventional methods of restoration include a removable complete denture, a removable partial denture, a fixed prosthesis, or combinations of these approaches. There are different indications for each method, with associated advantages and disadvantages. Removable dentures have long been considered problematic because of their varying mobility/stability over time and the inconvenience of removing them each day. Also, many removable dentures were bulky, others complicated chewing, and some were not adequately esthetic. Fixed prostheses were considered more esthetic and comfortable for the patient, but they involved the preparation of adjacent teeth and were associated with problems such as secondary decay or irreversible pulpitis. If the adjacent teeth did not have restorations, the decision to prepare them for a fixed prosthesis was difficult because two or more natural teeth would have to be surgically altered to provide retention for one or more artificial teeth (a bridge).

For centuries people have attempted to replace missing teeth by implanting synthetic and natural substances. **Implantation** has

been defined as the insertion of any object or material, such as an **alloplastic** substance or other tissue, either partially or completely, into the body for therapeutic, diagnostic, prosthetic, or experimental purposes. Implantation is usually differentiated from other, similar procedures, such as **replantation** and *transplantation*. Replantation refers to the reinsertion of a tooth back into its jaw socket after its accidental or intentional removal, whereas transplantation is the transfer of a body part (homogeneous or heterogeneous) from one host to another.

CRITICAL QUESTION

How did the concept of implantation evolve into a widely used restorative technique in dentistry?

History of Dental Implants

Dental implants began as far back as the early Greek, Etruscan, and Egyptian civilizations, employing various designs and materials ranging from jade and other stones and metals to bone and ivory. Some of the design concepts used then have evolved into the implants of today.

Seashells were used in place of teeth in 600 CE, evidence of which was found in Honduras, and tooth restorations made of jade and turquoise were found in Mayan skulls. Albucasis de Condue (936–1013) of France used ox bone to replace missing teeth; this was one of the early documented placements of implants. Through the centuries, various tooth transplants made of either human or animal teeth were tested. These transplants became status symbols, and they quickly replaced other artificial alternatives for restoring missing teeth. Toward the 18th century, Pierre Fauchard and John Hunter further documented tooth transplantation and specified conditions for the success of this procedure. They claimed that success was greater with anterior teeth, premolar teeth, and transplants placed in young people with healthy tooth sockets. Failure was believed to be the result of the incompatibility of the type of tooth used or the lack of conformity of the tooth to the socket.

The recognition of failure rates of transplants increased interest in the implantation of artificial tooth roots. In 1809 Maggiolo fabricated gold roots that were fixed to teeth by means of a spring. These gold implants were placed into fresh extraction sites, although they were not truly submerged into bone. The crowns were placed after healing had occurred around the implant. Many attempts followed. Harris (1887) proposed the use of a platinum post coated with lead. The post was shaped like a tooth root, and the lead was roughened for retention in the socket. Bonwell (1895) implanted gold or iridium tubes to restore a single tooth or support complete dentures. Payne (1898) implanted a silver capsule as a foundation for a porcelain crown that was cemented weeks after. Scholl (1905) demonstrated a porcelain corrugated root-shaped implant that lasted for 2 years and was anchored to adjacent teeth by pins. Greenfield (1913) introduced and patented a hollow “basket” implant made of a meshwork of 24-gauge iridium-platinum wires soldered with 24-karat gold. This device was used to support single implants and fixed dental prostheses (FDPs) comprising as many as eight implants.

Consistent problems with these artificial implant designs and materials supported the need for a scientific approach to implant selection and placement. Some have proposed that the “modern era” started in 1925 with the invention of the tubular extension implant by H. Leger Dorez. This implant allowed for an expansion of the screw in bone, leading to actual bone anchorage and initial stability. In 1937 Venable et al. investigated the interactions of cobalt alloy and other available metals and alloys with bone for use in dentistry. They concluded that certain metals produced a galvanic reaction, which led to corrosion when these metals contacted tissue fluids. They proposed the use of Vitallium, a cast alloy, which was composed of cobalt, chromium, and molybdenum. This alloy was considered to be relatively inert, compatible with living tissue, and resistant to the adverse reactions with body fluids. Vitallium has also been used in different forms of surgical devices, such as dental **subperiosteal implant** and orthopedic plates, screws, nails, and joints. Early evaluations documented Vitallium implants with survival times of 10 or more years.

The background of research, development, and applications of biomaterials for dental implants began with the application of available substances, often of metallic origin. Some separate the period before 1950 as an era of applications driven by need and availability. Examples include the early use of wires, pins, and rods fabricated from gold and other noble metals and alloys. In the 1950s, the cobalt-based alloys were cast and finished for subperiosteal and some root-form designs. The austenitic iron-based stainless steels constituted from iron-chromium and nickel

(sometimes with molybdenum as well) were also used in wrought and machined conditions. Within a decade, titanium and other reactive-group metals—plus carbons, ceramics, and eventually polymers—were considered.

The more “modern” era of biomaterials arose by the 1970s, when materials known and tested in many disciplines were constituted, fabricated, and finished as biomaterials. Consensus standards rapidly evolved for these biomaterials, which resulted in more consistent control of their properties. A very important aspect of this evolution—which included biomaterials, designs, and clinical application—was the clinical research led by P. I. Brånemark in Sweden. His studies used unalloyed titanium, now known as *commercially pure titanium* (CPTi); a root-form design; and very controlled conditions for surgery, restoration, and maintenance. Data presented in literature reviews and consensus conferences over the period 1972 to 2002 have demonstrated significant improvements in dental implant survival statistics. When outcomes were evaluated by objective criteria, the average survival at 5 years was about 50% in the 1970s. Since the 2000s, average survival at 10 years has been above 90% for these types of implants.

Classification of Implants

Implants can be classified according to anatomical location and device design, implant properties, or implant attachment mechanism.

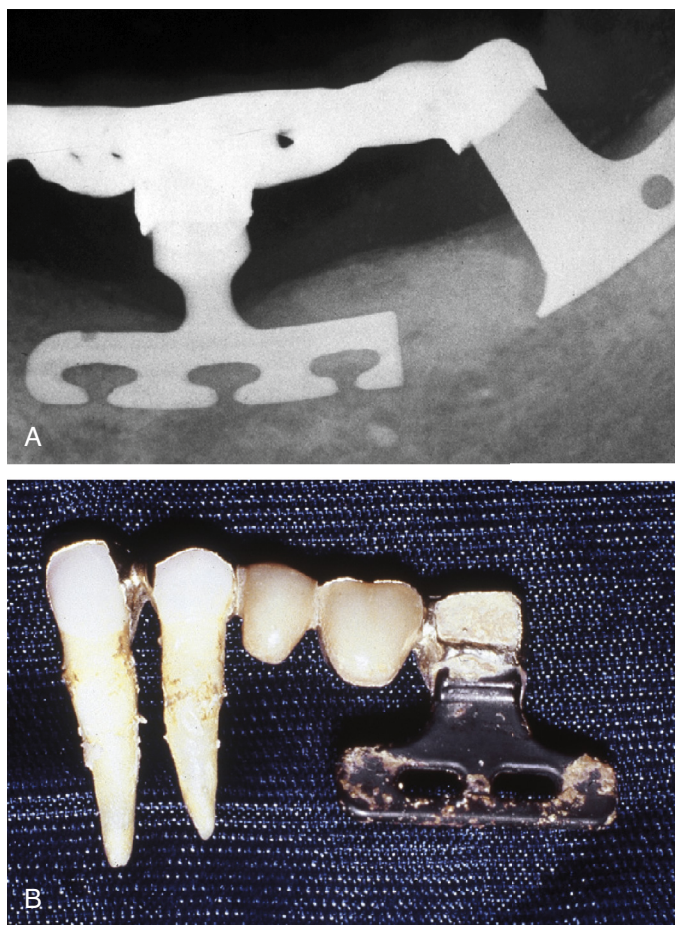
Anatomical Location and Implant Device Design

The first and most commonly used type of design is the **endosteal** (also called *endosseous*) **implant**, a device placed into an alveolar and/or basal bone of the mandible or maxilla that usually transects only one cortical plate. These implants were formed in many different shapes, such as root-form cylindrical cones or screws. They also came as thin plates called *plate* or *blade forms* and were used in all areas of the mouth. One example of an endosteal implant was called the *blade implant* (Figure 12-1), which was developed independently in 1967 by two groups led initially by Roberts (1970) and Linkow (1968). Endosteal blade implants consisted of thin plates placed into bone; they were most commonly used for narrow anatomical structures, such as posterior edentulous areas, after significant resorption of bone. Because of various issues with blade implants, their application in more recent implantology has decreased. Another example of an endosteal implant was the ramus frame implant (Figure 12-2), a horseshoe-shaped stainless-steel device inserted into the ascending rami (bilateral) and the anterior symphysis area of the mandible. As with the blade implants, the number of applications was limited. The most popular endosteal implant has been the root-form (Figure 12-3), which was designed initially to mimic the shape of tooth roots for directional load distribution and for positioning in bone. In longitudinal studies, the root-form implant has the most documentation of the endosteal implants, although several surgical stages may be needed for completion.

CRITICAL QUESTION

What are the indications for the use of mini-implants in dental practice?

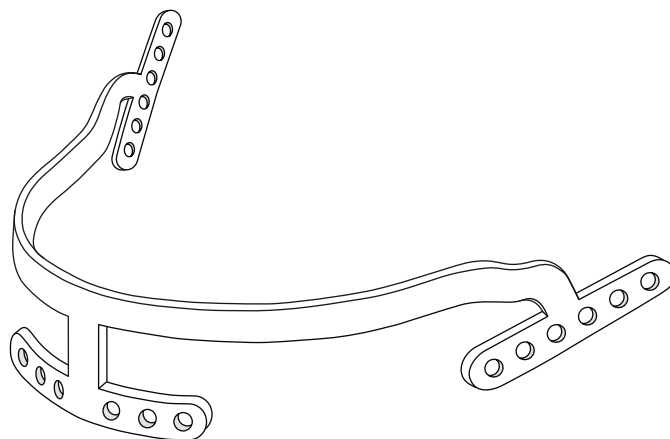
A mini-implant is a type of endosteal implant with some indications in dentistry. More notably, their use in orthodontics for appliance anchorage has increased. Other uses include overdenture



• **Figure 12-1** A, Blade implants embedded in bone, with some bone loss. B, Failed blade implant prosthesis that was also attached to natural teeth. (Courtesy Dr. Mickey Calverley.)

retention in areas where there is minimal bone available or in areas that are narrow. They can also be used to anchor temporary prostheses in the case of overdentures on an arch with newly extracted teeth. These implants were initially used as temporary implants, which helped anchor the prosthesis while the larger-diameter implants were left to osseointegrate. They could then be removed once the final prosthesis was fabricated. Over time, the success of these mini-implants has led to their evolution as final restorations for compromised cases. The diameter of mini-implants ranges from 1.8 to 2.9 mm (Figure 12-4). Most mini-implants can be placed without having to reflect a flap in the gingival tissue because of their small diameter. Mini-implants are also designed for immediate loading, offering the convenience of few visits and allowing the patients to have their prosthesis immediately. Although these implants are essentially made from the same material as the larger standard implants and are constructed as root-form implants, the main difference lies in their smaller diameter. This smaller size allows placement of these implants in areas where standard implants would normally require a bone-grafting procedure, which results in additional trauma and expense to patients. As the applications of mini-implants continue to grow, they are slowly being incorporated for use with FDPs, adding additional support in the pontic areas.

The second implant design is the subperiosteal implant (Figure 12-5), which employs an implant substructure and



• **Figure 12-2** Ramus frame blade implant that traverses entire mandible and attaches to ramus.

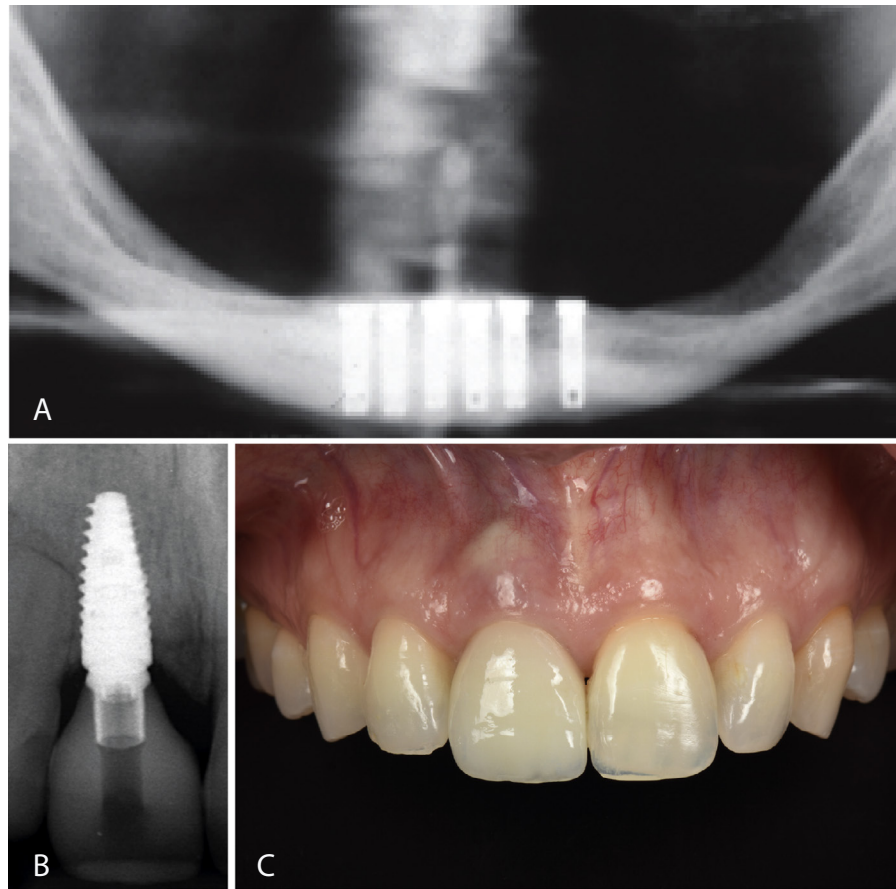
superstructure. The custom-cast frame was placed directly beneath the periosteum overlying and fitting along the bony cortex. This implant was first developed by Dahl (1943) and refined by Berman (1950), who used a direct-bone-impression technique. These devices were used to restore partially dentate or completely edentulous jaws when there was inadequate bone for endosseous implants. Use of the subperiosteal implant has been limited because of numerous considerations, including the difficulty of retrieval.

The third design is the **transosteal implant** (Figure 12-6), which combines subperiosteal and endosteal components. This type of implant penetrates both cortical plates and passes through the full thickness of the alveolar bone. Use of the transosteal implant has been restricted to the anterior area of the mandible and provides support for tissue-borne overdentures. The concept of transosseous implants was first conceived in Germany in the early 1930s; early examples were made of a cobalt alloy. Small (1968) developed the mandibular staple implant made of a titanium alloy, which was modified by Bosker (1983), who produced the transmandibular implant (TMI) made of a gold alloy. Other names for transosteal implants have included *staple bone implant*, *mandibular staple implant*, and *transmandibular implant*.

The fourth implant design is the **epithelial implant**, which is inserted into the oral mucosa. This type was associated with a simple surgical technique where the mucosa was used as an attachment site for metal inserts placed into an acrylic denture. Several disadvantages are associated with the epithelial implant, most notably a painful healing process and a requirement for continuous wear. The current use of “mucosal inserts” or epithelial implants is very limited.

Some oral implantologists also include the endodontic stabilizer as an anatomy-specific application system. These smooth or threaded pins (or screws) were placed through endodontically treated teeth with the implant extending into the bone. They were constructed from alloys or ceramics made of alumina or zirconia. Reported difficulties included sealing the transition zone from tooth to bone and the limited strength of small-diameter pins or screws.

From a historical and applications perspective, these systems were reviewed by Natiella et al. (1972) and subsequently in each decade by researchers who participated in professional society-based consensus conferences. To summarize the various biomaterials and designs tested for dental implants, examples of devices



• **Figure 12-3** A, Endosteal implants are placed directly into bone; they mimic root forms for proper placement and location in bone. B and C, Restored anterior implant blending well with adjacent teeth. (B and C, Courtesy Drs. Will Martin and Luiz Gonzaga.)



• **Figure 12-4** Mini-implants used for orthodontic anchorage, showing 2-mm diameter of the mini-implants compared with the 4-mm diameter of standard implants.

received for examination prior to 1990 are shown in Figures 12-7 through 12-9.

Implant Properties

Implant biomaterials can also be classified according to their composition and their physical, mechanical, chemical, electrical, and biological properties. These classifications often include ranked comparisons of properties, such as elastic moduli, tensile strength, yield strength, and ductility, to determine optimal clinical applications (Table 12-1). These properties are used to aid in the design

and fabrication of the prosthesis. For example, the elastic modulus of the implant is inversely related to the strain present at the implant–tissue interface during loading of the implant; that is, the greater the elastic modulus of an implant, the greater the stress in the implant and the lower the stress distributed to bone.

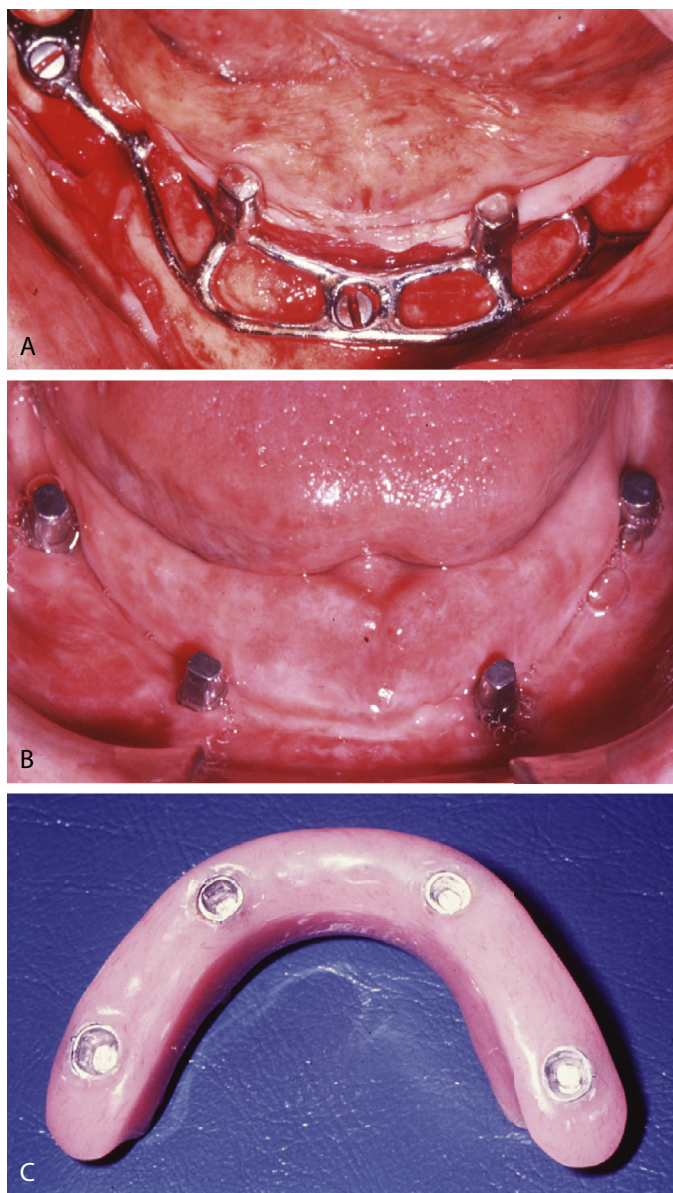
An implant material with an elastic modulus comparable to that of bone should be selected to produce a more uniform stress distribution across the interface. Ductility is another important property because this relates to the potential for some plastic deformation of abutments or fixtures without fracture in areas where there is high tensile stress. Metals possess both high strength and ductility, whereas the ceramics and carbons are brittle materials.

CRITICAL QUESTIONS

What is the preferred implant-to-tissue interaction? How has this influenced the popularity of implant applications?

Implant Attachment Mechanism

Periodontal structures, which attach teeth to bone, consist of highly differentiated fibrous tissue. These fibers are replete with numerous cells and nerve endings that allow for functional force transfer, sensory function, bone formation, and tooth movements. Although this is the ideal form of integration, there are no known implant biomaterials or designs at present that can stimulate the

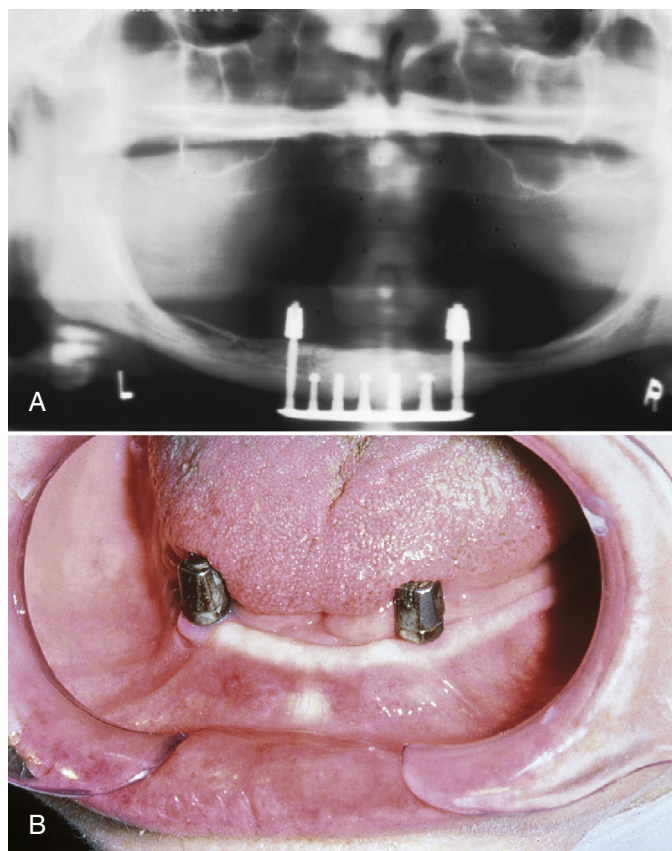


• **Figure 12-5** A, Subperiosteal implant positioned beneath the periosteum. Impression making often requires a difficult surgical technique. B, Superstructure for subperiosteal implant allowing for attachment of prosthesis. C, Denture prosthesis for subperiosteal implant. (Courtesy Dr. Joseph Cain and Dr. Richard Seals.)

growth of these fibers and can fully mimic the function of the periodontal ligament and a natural tooth.

In the past, implant attachment to fibrous connective tissue was accepted as a measure of successful implant function (the pseudoligament concept). This type of interaction was reported to be very susceptible to acute or chronic inflammatory responses, which were accompanied by pain and eventual loss of the implant. This type of attachment has also been called a *pseudoperiodontium*. Despite numerous reports of implant success, clinical studies indicate that this type of interaction is susceptible to progressive loosening and infection, with subsequent loss of the implant construct.

In contrast to the pseudoperiodontium, the implant-to-bone interaction (called **osseointegration**) is characterized by direct contact between bone and the surface of a functional implant after 1 year. This central theme of the Brånemark group was called



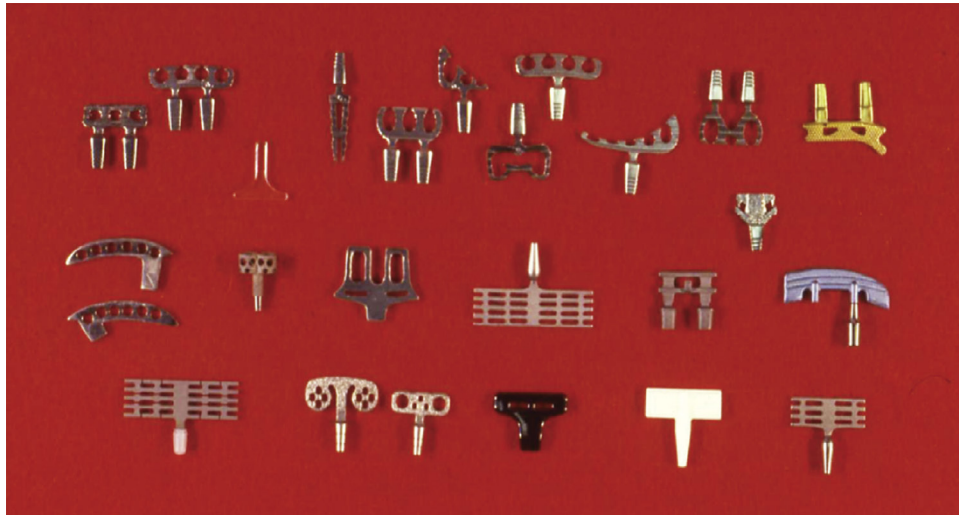
• **Figure 12-6** A, Panoramic radiograph of a transosteal implant showing perforation of both cortical plates, hence the name *staple implant*. B, Transmucosal abutment for transosteal implant allowing for placement of denture restoration. (Courtesy Dr. Joseph Cain and Dr. Richard Seals.)

“direct anchorage to bone” and has become a major attribute of dental implants. This mode is described as the direct adaptation of bone to implants without any other intermediate non-bony tissue and has been described by some as similar to tooth **ankylosis**, where no periodontal ligament or fibrous tissue exists. The strength of this contact has been shown to be stable, which is advantageous compared with the soft tissue interface described previously.

This type of osseous interface has been described extensively and includes a process wherein bone-producing cells migrate along the implant surface through the connective tissue scaffolding that forms adjacent to the implant surface. Integration at the implant interface is highly dependent on the implant surface’s chemistry and design. Bone apposition has been reported at higher rates when microscopic surface ridges are present. Osseous integration has also been achieved through the use of **bioactive** materials that stimulate the formation of bone along the surface of the implant. Another way of achieving osseous integration involves de novo bone formation, wherein a mineralized interfacial matrix and/or active growth factors are deposited along the implant’s surface. The implant’s surface topography and chemistry influence the bone development around the implant.

CRITICAL QUESTION

What is the implication of having direct bone contact and the absence of a periodontal ligament on the prosthetic superstructure?



• **Figure 12-7** Collection of endosteal blade implant designs for restoring single or adjacent teeth.



• **Figure 12-8** Collection of endosteal implants for partial arch restorations.



• **Figure 12-9** Collection of different designs and materials used for endosseous implants.

Implant-supported restorations differ from tooth-supported restorations in that the former lack a periodontal ligament, which reduces shear stress and strain, provides shock absorption, and reduces the development of dangerously high occlusal forces. The benefits of the periodontal ligament reduce the potential for

inadvertent damage to the tooth or restoration. Ceramic materials are brittle by nature, and because of inherent processing flaws, they cannot withstand any stress above their yield point, which is equivalent to their tensile strength. These stresses can be generated during occlusal loading. Implants, on the other hand, are directly anchored to the bone and cannot readily flex laterally under extremely high occlusal loads to relieve some of the excessive loading. [Vult von Steyern et al. \(2005\)](#) analyzed the fracture strength of all-ceramic prostheses on abutment teeth and implants in vitro. They concluded that implant-supported ceramic prostheses fractured at higher loads than those supported by natural teeth because of the lack of a periodontal ligament. This indicates that the supporting structures, in this case the implants, are subjected to higher stress levels. However, clinical studies have shown that the complication rate for implant-supported FDPs is 30% over 5 years, whereas that for tooth-supported FDPs is 27.6% over the same time period, indicating no real difference in survival of the restoration between the two types of support.

Conversely, studies have analyzed whether the type of prosthetic material can affect the longevity of an implant. Bränemark and Skalak advocated the use of acrylic for the prosthetic superstructure to act as a shock absorber and essentially dissipate the load on the implants and the bone surrounding them. Acrylic, noble metal alloys, and ceramic are being used in implant superstructures. In the absence of a periodontal ligament, minimizing the load along the bone-implant interface is logical. However,

TABLE 12-1 Mechanical Properties and Density of Metallic and Ceramic Implant Materials

Material	Grade or Condition	Yield Strength (MPa)	Elongation (%)	Modulus of Elasticity (GPa)	Tensile Strength (MPa)	Density (g/cm ³)
CP titanium	1	170	24	102	240	4.5
	2	275	20	102	345	4.5
	3	380	18	102	450	4.5
	4	483	15	104	550	4.5
Ti-6Al-4 V		860	10	113	930	4.4
Ti-6Al-4 V ELI		795	10	113	860	4.4
Ti-15Zr		953		103.7		
Co-Cr-Mo	Cast	450	8	240	700	8.0
	Annealed	190	40	200	490	8.0
	Cold-worked	690	12	200	860	8.0
Aluminum oxide	Polycrystalline	400* (500/flexure)	0.1	380	220	3.96
Zirconium oxide	Y ₂ O ₃ (stabilized)	1200 (flexure)	0.1	200	350	6.0
Cortical bone		N/A	1	18	140	0.7
Dentin		N/A	0	18.3	52	2.2
Enamel		N/A	0	84	10	3.0

*ASTM Standard: minimum values.

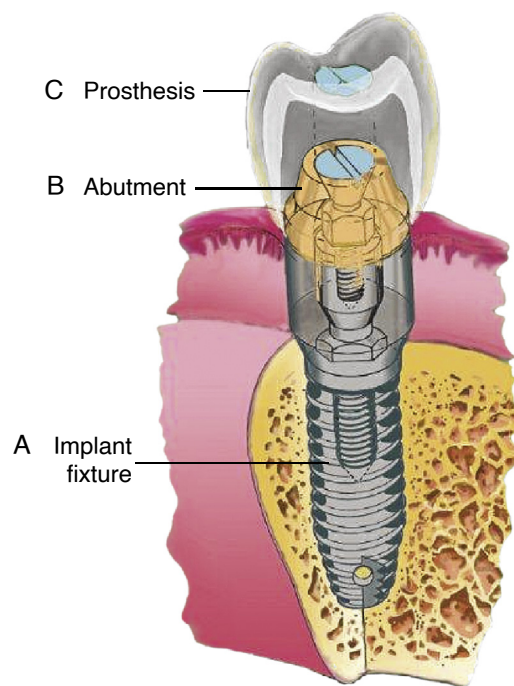
there is no evidence to associate the use of any prosthetic material with the longevity and survival of the implants.

CRITICAL QUESTION

What is the purpose of pretreating implant surfaces?

Implant Components

To understand the material characteristics and function of an implant, one must first be knowledgeable about the numerous component parts. Although each implant system varies, the parts are basically consistent. The body of the implant (called a *fixture* for the Brånemark system) (Figure 12-10, *A*) is the implant component that engages with bone. Depending on the implant system, the body section can have different surfaces—threaded, grooved, perforated, plasma-sprayed, sand-blasted, or coated. These characteristics are often classified as subtraction (threading, grooves, perforations, sand-blasting, or acid-etching) or addition (plasma spray and coating) types. Each surface type is meant to enhance bone integration and primary stability; that is, increased surface area enhances bone integration, and better cortex engagement plays an important role in immediate and long-term bone anchorage. The coated or plasma-sprayed biomaterials, discussed later in this chapter, are used to enhance attachment to bone. The second component (Figure 12-10, *B*) is the transmucosal abutment, which provides the connection



• **Figure 12-10** Diagram of implant components. **A**, The implant fixture (endosteal root-form). **B**, Transmucosal abutment serving as the attachment between fixture and the actual prosthesis. **C**, The actual prosthesis, which can either be cemented, screwed, or swaged.

between the implant body and the intraoral prosthesis to be fabricated (Figure 12-10, C), which will provide intraoral function. The abutment is usually connected to the implant body by means of a screw; however, the abutment can also be cemented or connected by a Morse taper-type design. Abutments can become engaged to the implant body either by an internal or external geometry (initially a hexagon) within the implant body, which also serves as an antirotation device and is particularly important for single-unit restorations. The last part of an implant is the prosthesis. The prosthesis can be attached to the abutments through the use of screws, cement, precision attachments, magnets, or other designs, such as those used for removable implant overdentures.

Implant Surgical Placement

Placement and restoration of implants intended to integrate with bone are usually performed in stages. The first stage, or stage 1, occurs when the implant is surgically placed into the bone (Figure 12-11). The implant is left within the bone (passive) for a period of months, depending on the bone quality, and allowed to heal and become integrated. A secondary surgery, or stage 2, is sometimes required whereby the implant is uncovered and exposed through the oral environment (Figure 12-12). This exposure is performed

4 to 6 months after implant placement and after proper bone healing has occurred.

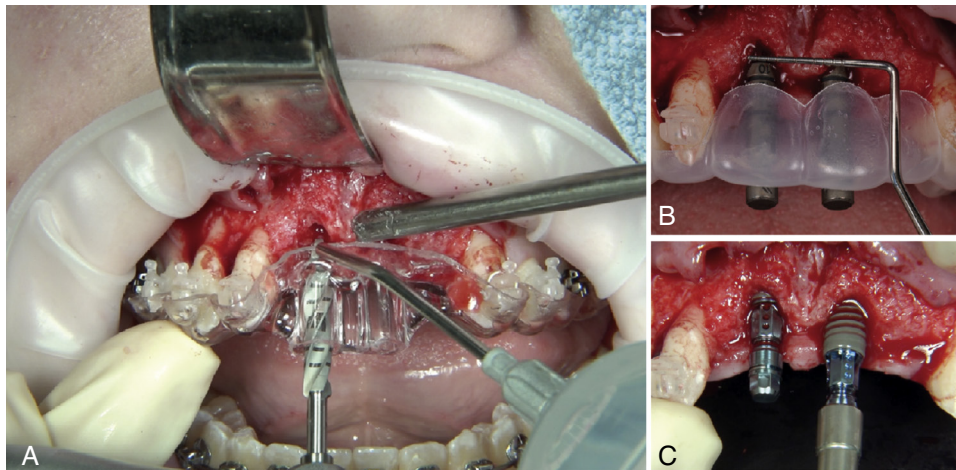
The restorative phase then follows the placement of abutments and a crown, a partial denture, or a removable denture, with or without a bar construct. Some implant systems use only one surgical intervention, where the implant is immediately placed in contact with the oral environment and is sometimes able to function in a limited way within days. Some of these systems have even been advocated for immediate functional loading, with reports of relative success.

CRITICAL QUESTIONS

When can an implant restoration be considered successful? What criteria are used to determine this success? What clinical situations can affect the success rate of dental implants?

Evaluation of Clinical Success

There have been several long-standing debates about what is considered successful in implant dentistry. Some consider that the encapsulation of an implant with a pseudoperiodontium is a successful implant condition. The most frequently cited success



• **Figure 12-11** Implant placement, Stage 1 surgery. **A**, Sequential twist drills used for osteotomy. **B**, Depth pins used to confirm osteotomy and implant parallelism. **C**, Implant placement following the correct angulation. (Courtesy Dr. Luiz Gonzaga.)



• **Figure 12-12** Implant placement, Stage 2 surgery. **A**, Tissue evaluation pre uncovering. **B**, Healing abutment on implant after uncovering. Minimal crestal incision, tissue punch or laser can be used as long as keratinized mucosa is present. **C**, Impression coping on implant to facilitate fabrication of provisional restoration at the same appointment. (Courtesy Dr. Luiz Gonzaga.)

criteria from the 1970s are those in the publication edited by [Schnitman and Schulman \(1979\)](#). More recently, summaries from [Cochran and Fritz \(1996\)](#) and [Albrektsson et al. \(1986 and 1991\)](#) are often cited.

Criteria of Success

Proposed early requirements included (1) implant mobility less than 1 mm when tested clinically; (2) no evidence of x-ray radiolucency; (3) bone loss less than one-third the height of the implants; (4) absence of infection, damage to structures, and violation of body cavities—inflammation, if present, must be amenable to treatment; and (5) a success rate of 75% or more after 5 years of functional service using objective criteria for evaluation. As an example, these conditions were somewhat different from the criteria of [Albrektsson et al. \(1986\)](#), which included the following: (1) the implant must be immobile when tested clinically; (2) there must be no evidence of periapical x-ray radiolucency; (3) vertical bone loss should be less than 0.2 mm annually following the implant's first year; (4) absence of signs and symptoms such as pain, infections, neuropathies, paresthesias, or violation of the mandibular canal; and (5) a success rate of 85% or more at the end of a 5-year observation period and 80% at the end of a 10-year period when evaluated by objective criteria for success.

Smith and Zarb (1989) recommended an addition to Albrektsson's criteria by stating that the patient's and dentist's satisfaction should be the primary consideration and that esthetic conditions should be met. Patient satisfaction and patient attitude toward the prosthesis have been included in some subsequent lists of criteria for success. Although these criteria have become more stringent in recent years, success in implant dentistry is still difficult to quantify.

In 2008, the International Congress of Oral Implantologists arrived at a consensus for rating implant success, survival, and failure. The scale ranges from 1 to 4, with 1 being deemed successful and optimal health and 4 as clinical failure. The consensus evaluates the presence of pain or tenderness, mobility, bone loss, and exudate history ([Table 12-2](#)).

Standardized criteria for success should continue to evolve to enable proper evaluation of implant dentistry as the systems and treatments change over time.

Evaluation of Failure

Most recently, there has been much focus on peri-implant diseases because the diagnosis of these has never been fully established. As such, implant failures resulting from peri-implantitis range anywhere from 11% to 55%, and the true prevalence of this disease is elusive. *Peri-implantitis* and *perimucositis* are defined as mucosal inflammation surrounding the implant with or without 2 mm or more of bone loss after restoration (implant loading). The incidence of perimucositis and peri-implantitis on patients who receive implants varies from 20% to 90% within a period of 5 to 11 years. There are no definitive interventions associated with successful therapy of peri-implant disease. With more and more implants being placed in lieu of traditional fixed and removable dental prosthesis to replace missing teeth, peri-implantitis is becoming a major dental health issue. In 2017 the World Workshop on the Classification of Periodontal and Peri-Implant Diseases and Conditions was convened to outline proper identification of peri-implant diseases. The

TABLE 12-2 International Congress of Oral Implantologists Health Scale for Rating the Success or Failure of Dental Implants

Quality Scale	Clinical Condition
I. Success	No pain or tenderness at function 0 mobility <2-mm bone loss No exudate history
II. Satisfactory	No pain or tenderness at function 0 mobility 2- to 4-mm bone loss No exudate history
III. Compromised	May have pain or tenderness at function 0 mobility >4-mm bone loss and <1/2 implant length No exudate history
IV. Failure	Pain or tenderness at function Mobility Bone loss >1/2 implant length Uncontrolled exudates No longer in the mouth

From Misch CE, et al: Implant success survival and failure: International Congress of Oral Implantologists, Pisa, Italy, Consensus Conference, *Implant Dent* 17:5–15, 2008.

diagnostic criteria for peri-implant diseases are shown in [Table 12-3](#). Although the causes of peri-implantitis and peri-mucositis are still being investigated, there is a strong link between the incidence of the disease and chronic periodontitis, poor plaque control, and absence of regular implant maintenance. The links between systemic risk factors, such as smoking and diabetes, were found to be inconclusive.

CRITICAL QUESTION

What is the primary mechanism of failure involved with dental implants?

Longevity of Dental Implants

The popularity of dental implants to restore full or partial edentulism has been the result of predictable outcomes with high success rates. Five-year success rates of 96% to 98% are reported for mandibular implants and 94% to 96% for maxillary implants, depending on the quality of bone, surgical technique, and primary implant stability. Implant failure can occur at an early stage or a late stage. Early-stage failures occur prior to loading or placement of the prosthesis and are most commonly associated with poor surgical techniques or inability to achieve primary stability.

Brånemark and Albrektsson reported strict protocols required to achieve proper osseointegration. These include following proper aseptic techniques and allowing the bone to heal around the implant for a period of 4 to 6 months. The healing process allows the bone to be generated around the implant free from bacteria and **micromotion**, which can disrupt bone deposition around the implant. Micromotion above 150 μ m has been shown to promote soft tissue deposition and eventual encapsulation of the implant body with fibrous tissue. This occurrence is classified

TABLE 12-3 Classification of Periodontal and Peri-Implant Diseases and Conditions

	Peri-Implant Soft Tissue Inflammation (Redness, Swelling, Profuse Bleeding on Probing)	Additional Bone Loss After Initial Healing	Probing Depth
Peri-implant health	None	None	None
Peri-implant mucositis	Present with line or drop of bleeding within 30 seconds after probing	None	None
Peri-implantitis	Present	Radiographic evidence of bone loss after initial healing*	Increased probing depth compared with probing depth at delivery of prosthesis

*In the absence of baseline radiographs, a combination of bone loss ≥ 3 mm, bleeding on probing, and probing depth ≥ 6 mm is indicative of peri-implantitis.

as a failure of osseointegration. Allowing the bone surrounding the implant to heal necessitates a two-step surgical technique for implant placement, as mentioned earlier. In 1990 Schnitman et al. reported on the success of immediate loading of dental implants. This technique eliminates the need for a second surgery and allows the implant to be used immediately to support a temporary or permanent prosthesis (Figure 12-13). There are mixed results regarding the success rates between immediately loaded and conventionally loaded implants. Although the success rates vary, there is a consensus that immediate loading constitutes a more technique-sensitive process and patient-selective endeavor. Researchers conclude that if these guidelines are followed, the success rates for immediately loaded implants are more favorable. As with conventional implants, primary stability is important in achieving proper osseointegration. The problem with immediately loading implants is that micromotion can occur and jeopardize the bone formation around the implant body. However, research has shown that there is a range of allowable micromotion from 30 to 150 μm , where bone deposition is not hindered. The advantage of immediate loading is shorter treatment time, which leads to greater patient convenience and comfort by reducing the number of surgeries and allowing the immediate placement of a prosthesis.

Late-stage failures occur after loading or placement of a prosthesis and can be the result of complications stemming from uncontrolled periodontal disease or overloading of the implant. Overloading can be caused by lateral or oblique forces exerted on the prosthesis from improper occlusal loading or parafunctional habits. Bone is susceptible to microfractures or fatigue fractures, depending on the type and amount of occlusal load being exerted. Once the bone reaches the tolerance limit for the occlusal loads, these fractures can occur and can lead to implant failure. Excessive bone deformation has been shown to occur between 2000 and 3000 microstrain units, and pathological overloading can be seen at over 4000 microstrain units. One thousand (1000) microstrain units equals 0.1% deformation.

CRITICAL QUESTION

Which factors in the implant and prosthesis design affect the load transfer to bone?

A delicate balance must be achieved in load transfer from implant to bone to maintain proper bone health. Excessive occlusal forces lead to overloading of the bone surrounding the implant,

which can, in turn, lead to bone resorption and microfracture. Conversely, minimal load transfer to bone can lead to bone atrophy from disuse. Rough surfaces along the implant are typically conducive to transferring more load to the bone as a result of the increased surface-area contact. An increase in contact area also reduces localized stress. This reduction in localized stress decreases the strain around the implants. On the other hand, smooth-surfaced implants have the opposite effect, as evidenced by resorption along the marginal areas, where there is a smooth transition from the implant to bone.

The type of prosthesis used can also influence how the forces are transferred along the implant–bone interfaces. Prosthesis design should minimize long cantilever arms to avoid offset loads or high bending moments on the implants. Lateral forces are not tolerated as well as direct axial loading. Cement-retained prostheses have been found to be more favorable in maintaining proper axial loading as opposed to screw-retained restorations. The absence of a screw hole allows proper occlusal design for the prosthesis to adequately direct loading to the implant. Conversely, the presence of a screw hole will redirect occlusal forces and introduce bending moments to the implant.

CRITICAL QUESTION

Which biomaterial is best for certain types of implants?

Implant Biomaterials

The most commonly used implant materials are made from metallic biomaterials. Implants also differ in their surface condition. Some implants are machined and finished; others are coated with different types of biomaterials. Of the four types of implants by design, endosteal implants are the most commonly used for dental applications. Thus the nature of the biomaterials used for endosteal implants is a central focus of the following discussion.

Metallic Implants

Three metallic-based systems have been used to make dental implants: CPTi and titanium alloys, stainless steel, and cobalt-chromium-molybdenum alloys. These metallic implants undergo one or more of several surface treatments prior to final packaging for implantation. Some of these modifications include *passivation*, *anodization*, *ion implantation*, and *texturing* by several different



• **Figure 12-13** Immediate placement of dental implants. **A**, Fractured maxillary central incisor seen radiographically. **B**, Central incisor extracted. **C**, Implant placed immediately after extraction. **D**, Temporary abutment placed for temporary crown. **E**, Final restoration completed. (From Garg AK: *Implant Dentistry*, ed 2, St. Louis, 2010, Mosby.)

methods. Passivation refers to the enhancement of the oxide layer to minimize the release of metallic ions as a result of surface transfers. Minimization of ion release contributes to *biocompatibility*. Passivation treatments can be performed through immersion in 40% nitric acid or anodization, a process by which an electrical current is passed through the implant when it is placed in a specialized solution. The former method of treatment minimally increases the thickness of the oxide layer, whereas the latter treatment can result in a thicker oxide layer, which has been shown to be beneficial in enhancing corrosion resistance. Surface texturing increases the surface area of the implant and enhances tissue interactions by increasing the area through which stresses are transferred to bone. This is accomplished by several methods, including plasma spraying, acid-etching, and blasting with aluminum oxide or another ceramic or ceramic-like material. Plasma spraying involves melting materials under high temperatures and

then spraying the material onto the surface of the implant. This method can be used with Ti or various ceramic coatings, as discussed later in this chapter. The increased implant surface area should remain passive because a greater surface area influences the overall release of metallic ions. Another surface modification for the implant is ion implantation, which consists of bombarding the implant surface of the implant with high-energy ions up to a surface depth of a few micrometers. This procedure has been claimed to increase the corrosion resistance of the titanium alloys through the formation of a titanium nitride (TiN) surface layer if the ion is nitrogen.

Titanium and Titanium Alloy

Titanium exists in nature as rutile (TiO_2) or ilmenite (FeTiO_3) compounds and requires specific extraction methods to be recovered in the elemental state. Titanium has several favorable physical

properties, which include a low density of 4.5 g/cm^3 and a relatively high flexure strength comparable to that of cast forms of cobalt and stainless-steel alloys. Titanium is very resistant to corrosion because of a passivating layer of titanium oxide, which is formed instantly on the surface. A new oxide layer re-forms on the surface as soon as this oxide is lost because of mechanical removal. This oxide layer can slowly become thicker over time and can reach a maximum of 25 nm in 4 years. In vitro, this layer can be removed by using corrosive acids or ion-etching. Pure titanium has the ability to form several oxides, including TiO , TiO_2 , and Ti_2O_3 . Of these, TiO_2 is considered the most stable and is found after exposure to physiological conditions.

The most commonly used titanium products are grades 1 to 4 of CPTi. Titanium alloys, namely, Ti-6Al-4V and Ti-6Al-7Nb, are used in extra-low interstitial (ELI) grades. The ELI contains low levels of oxygen dissolved in interstitial sites in the metal. Lower amounts of oxygen and iron improve the ductility of the ELI titanium alloy, which can be alloyed with different elements to modify its properties. As discussed in [Chapter 9, Titanium Alloys](#), alloying elements can be added to titanium alloys to stabilize either the α or β phase. Aluminum acts as an alpha stabilizer for the purpose of increasing strength and decreasing density. Vanadium and niobium are beta-phase stabilizers, which are used to minimize the formation of TiAl_3 to approximately 6% or less and to decrease the alloy's susceptibility to corrosion. Except for CPTi, the modulus of elasticity of Ti-6Al-4V is closer to that of bone than that of any other widely used metallic implant biomaterial. Newer titanium alloys have been developed, including Ti-13Nb-13Zr and Ti-15Mo-2.8Nb. These alloys use other phase stabilizers instead of aluminum and vanadium and may exhibit greater strength and corrosion resistance.

As listed previously, CPTi comes in different grades, from CP grades I to IV. The compositions of these metals in weight percentage are given in [Table 12-4](#). The strength of CPTi is less than that of Ti-6Al-4V alloy, although the modulus of elasticity values are comparable ([Table 12-1](#)). The table shows that Ti alloys maintain the fine balance between sufficient strength to resist fracture under occlusal forces and to retain a lower modulus of elasticity for more uniform stress distributions across the bone-implant interface.

Most recently, binary alloys such as Ti-Nb, Ti-Hf, and Ti-Ta have been examined for use as dental implants. Ti-15Zr was introduced clinically under the trade name Roxolid (Straumann, Basel, Switzerland) for use as narrow implants where regular-size

implants are not indicated. The claim is that these alloys are more biocompatible than the current Ti-6Al-4V alloy with the elimination of Al and V, which have been known to cause cytotoxic reactions and chromosomal damage. The Roxolid demonstrates improved mechanical properties, with a tensile strength of 953 MPa compared with 680 MPa for Ti-6Al-4V and 310 MPa for CPTi. There are limited studies on this material; however, these studies have shown that there is no cytotoxic behavior associated with this alloy, there is greater bone-implant contact (BIC) after 6 weeks of osseointegration, and it has similar elastic characteristics with the Ti-6Al-4V with higher strength. As with all implant materials, long-term clinical data are needed to fully ascertain risks and benefits.

Stainless Steel

Used in the form of surgical austenitic steel, these metals have 18% chromium for corrosion resistance and 8% nickel to stabilize the austenitic structure. Stainless steel is most often used in the wrought and heat-treated state and possesses high strength and ductility. Despite its low cost and ease of fabrication, this alloy is not widely used in implant dentistry because of a potential allergic response to nickel and a susceptibility to crevice and pitting corrosion. The corrosion products for stainless steel contain iron, chromium, nickel, and molybdenum. These elements or their ions can accumulate in the tissues surrounding the implant and subsequently be transported to other parts of the body to produce a potentially unfavorable response. Surface treatments such as surface passivation and ion implantation are used to improve the corrosion resistance, although austenitic stainless steels are still prone to localized attack in long-term applications.

Cobalt-Chromium-Molybdenum Alloy

This class of alloys generally consists of 63% cobalt, 30% chromium, and 5% molybdenum, with small amounts of carbon, manganese, and nickel. Molybdenum is a stabilizer, chromium provides the passivating effect to ensure corrosion resistance, and carbon serves as a hardener. Vitallium is the representative material of Co-Cr-Mo alloy, which was introduced by Venable in the late 1930s. This metal was initially shown to lack electrochemical activity and any tissue reaction. Ticonium, a Ni-Cr-Mo-Be alloy, was also used as a dental implant material, although this alloy revealed some adverse issues related to corrosion and biocompatibility. In later studies, Vitallium was associated with chronic inflammation and no osseous integration for several endosteal and subperiosteal

TABLE 12-4 Composition of CP Titanium and Alloys (Percent by Weight)*

Titanium	N	C	H	Fe	O	Al	V	Ti
CP grade I	0.03	0.08	0.015	0.20	0.18	—	—	Balance
CP grade II	0.03	0.08	0.015	0.30	0.25	—	—	Balance
CP grade III	0.05	0.08	0.015	0.30	0.35	—	—	Balance
CP grade IV	0.05	0.08	0.015	0.5	0.4	—	—	Balance
Ti-6Al-4 V alloy	0.05	0.08	0.015	0.3	0.2	5.50–6.75	3.50–4.50	Balance
Ti-6Al-4 V (ELI alloy)	0.05	0.08	0.012	0.25	0.13	5.50–6.50	3.50–4.50	Balance

*ASTM Standard: minimum values.

designs. To improve implant performance, inert biomaterials in the form of aluminum oxide and other ceramics were deposited on alloy surfaces. Aluminum oxide and zirconium oxide coated on cobalt alloys were found to have no effect on improving the biological acceptability of the implants evaluated. Co-Cr-Mo alloys have a high elastic modulus and resistance to corrosion. The additions of ceramic coatings such as calcium phosphate did not significantly alter the bulk portions of the alloy. Studies of cobalt alloys have shown that their lower ductility is a result of the agglomeration of compounds rich in carbon, chromium, and molybdenum. Also, studies have shown that ductility is improved by reducing the carbon content and controlling the processing of the alloy. Co-Cr-Mo and stainless-steel alloys continue to be used for some implants, such as subperiosteal and transosteal implants and ramus frames, because of their castability, mechanical properties, and lower cost.

Ceramic and Ceramic-Like Coated Metal Implant Systems

Several synthetic and biological materials have been used specifically for the treatment of bone defects, ridge augmentation, and osteoporotic lesions. These biomaterials can either be plasma-sprayed or blasted onto the metallic implant to produce ceramic-like surfaces, which can be more thermodynamically stable, hydrophilic, nonconductive of heat and electricity, and bioactive at the surface, thereby producing a high-strength integration with bone and the surrounding tissues. The term *bioactive* refers to a variety of inorganic biomaterials that can enhance integration with bone. These are generally brittle and may have high elastic moduli and low tensile strengths.

Recently, ceramic implants made from yttria-stabilized zirconia (3Y-TZP) were shaped into actual threaded implants and implant abutments. Ceramic implants can withstand only relatively low tensile or shear stresses induced by occlusal loads, but they can tolerate quite high levels of compressive stress (Table 12-1). Additionally, these implants have a more esthetic appearance than titanium, with increased wear and corrosion resistance. Aluminum oxide (Al_2O_3) is used as a standard biomaterial for ceramic implants because of its inertness (biostability), with no evidence of adverse in vivo reactions. Zirconia (ZrO_2) has also demonstrated a high degree of inertness. These types of ceramic implants are not bioactive in that they do not promote the formation of bone. This property is double-edged because this also minimizes bacterial affinity and therefore the incidence of peri-implantitis (see following discussion). These materials have high strength, stiffness, and hardness and function very well for some designs of dental implants. However, there have been limited clinical data on these zirconia implants, and some of the results have been catastrophic, with early fracture being much higher than the titanium implants for both the implants themselves and the abutments.

Of the synthetic types of materials, calcium phosphates are the most successful for grafting and bone augmentation. This performance is probably associated with the fact that bone is composed of 60% to 70% calcium phosphate. These materials are nonimmunogenic and are biocompatible with host tissues. The two most commonly used calcium phosphates are hydroxyapatite (HA) or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and tricalcium phosphate (TCP), $\text{Ca}_3(\text{PO}_4)_2$. Hydroxyapatite and tricalcium phosphate are used as bone-graft materials in granular or block form to

serve as a template for the formation of new bone. Because these materials are known to promote and achieve a direct bond of the implant to hard tissues, they are classified as bioactive. Both also promote vertically directed bone growth and a relatively strong bond to bone.

Bioactivity is defined in the ninth edition of the *Glossary of Prosthodontic Terms* as the “reactive potential of implant material that allows interaction and bond formation with living tissues; active potential depends on material composition, topography, and chemical or physical surface variations.” More specifically, the bioactivity of bone with an implanted material indicates the bond of bone to hydroxyapatite. HA, TCP, and other calcium phosphates are bioactive, in part, as a result of the release of calcium and phosphate ions within the surrounding tissue. Studies have revealed several differences in the tissue response to these materials after implantation. The beta form of TCP is resorbed more rapidly than HA and results in a breakdown of TCP. Some have reported a replacement of mesenchymal cells with features resembling osteoprogenitor cells. Studies have also shown that after 4 weeks of implantation, osteocytes accumulate adjacent to HA granules, indicating the possibility of osteogenesis with these implants. This is one of the justifications for using calcium phosphate compounds for coatings on implants placed into bone.

The use of these calcium phosphates as coating biomaterials for metallic implants is directly related to their physical and chemical properties. The more crystalline the HA coatings, the more resistant they are to clinical dissolution. A minimum of 50% crystalline HA is considered a preferable concentration for coatings. Dissolution of the coating occurs at a higher rate with the more amorphous structural conditions. Heat treatment after the deposition process improves the crystallinity of HA. The major advantage of these ceramic-like coatings is that they can stimulate the adaptation of bone and very often exhibit a more intimate bone-to-implant contact compared with a metallic surface. The amount of bone integration has been compared between metallic implants and ceramic-coated implants in numerous studies; these studies suggest that there is greater bone-to-implant integration with the HA-coated implants during the early stages of osseointegration. However, other studies indicate that there is no significant difference between the HA-coated and the uncoated implants after longer observation periods.

The bioglasses (SiO_2 - CaO - Na_2O - P_2O_5 - MgO) are another form of bioactive ceramic biomaterials. These materials are known to form a carbonated hydroxyapatite layer in vivo as a result of their calcium and phosphorus content. The formation of this layer is initiated by the migration of calcium, phosphate, silica, and sodium ions into tissue as a result of external pH changes. A silica-rich gel layer forms on the surface as elements are released. The silicon depletion initiates a migration of calcium and phosphate ions to the silica gel layer from both the bioglass surface and tissue fluids. This results in the formation of a calcium-phosphorus layer that stimulates osteoblasts to proliferate. These osteoblasts produce collagen fibrils that become incorporated into the calcium-phosphorus layer and are later anchored by the calcium-phosphorus crystals. This layer is 100 to 200 mm thick and has been shown to form a strong bone-bioglass interface. Bioglasses are classified as bioactive materials because they stimulate the formation of bone. They are more often used as grafting materials for ridge augmentation or bony defects than as coating materials for metallic implants because the interfacial bond strength of bioglasses with the metallic substitute and other

ceramic substrates is weak and is subject to dissolution *in vivo*. Despite their favorable **osteoinductive** ability, bioglasses are also very brittle, which makes them unsuitable for use for some stress-bearing implant applications.

Other Implant Materials

Carbon and a carbon compound (C and SiC) were introduced in the 1960s for use in dental implantology. Vitreous carbon, which elicits a very minimal response from host tissues, is one of the most biocompatible materials. Vitreous carbons are the result of the controlled thermal degradation of a preformed polymeric solid that leaves a relatively pure glassy carbon residue that possesses the glassy and ceramic properties of graphite. Studies have confirmed that the morphology of the bone–implant interface is similar to that associated with an HA implant. Compared with the metallic implants, carbon is more inert under physiological conditions and has a modulus of elasticity similar to that of dentin and bone. Thus carbon deforms at a rate similar to those tissues, enhancing the transmission of biomechanical forces. However, carbon is susceptible to fracture because of the brittleness and susceptibility of this material under tensile stress in the presence of surface flaws, which is usually generated as a component of flexural loading. Carbon-based biomaterials have also been used for ceramic-like coatings on metallic implants.

Critical Question

With the abundance of implant materials to choose from, how does a clinician know which biomaterial is best for a particular implant application?

Selecting an Implant System

Because of the abundance of different implant biomaterials and implant systems, knowing the indications for their use is important. Perhaps the most important consideration is the strength of the implant biomaterial and the type of bone in which the implant will be placed. The other factors to consider are the implant design, abutment choices, abutment availability, surface finish, and biomechanical considerations of restorative treatments.

Characteristics of the Material

The strength of an implant is often a consideration, depending on the area of placement. If the implant is located in a zone of higher force transfer (e.g., in the posterior area of the arch), the clinician might consider using a higher-strength material such as grade IV CPTi or one of the titanium alloys. Some controversy exists as to which titanium metal or alloy to use because some researchers believe that aluminum and vanadium can be toxic if released in sufficient quantities. Other considerations for selection include a history of implant fracture in the placement area of interest, the use of narrower implants, and a history of occlusal or parafunctional habits. Anterior implants, which are designated for use in narrow spaces, have smaller diameters, in the range of 3.25 mm or less. Conversely, single implants placed in posterior areas have larger diameters, up to 7 or 8 mm. Selection of the implant biomaterial must also be evaluated in terms of the abutment and intraoral biomaterials and dental materials. Electrochemical studies of the corrosion of metals now provide lists of acceptable and unacceptable combinations under conditions

where parts touch one another and galvanic corrosion might exist. In general, the titanium and cobalt alloys are relatively stable, and both have been combined electrochemically with the high-noble dental alloys. Base metal and amalgam combinations are a concern.

CRITICAL QUESTION

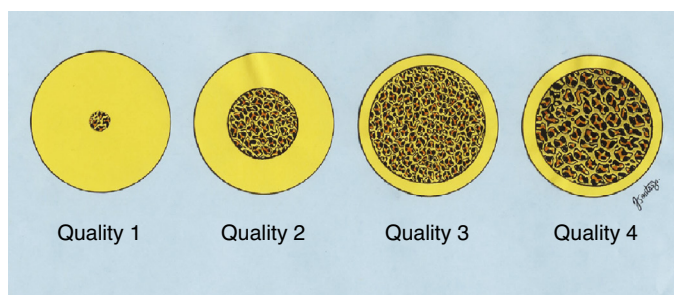
How do implant characteristics and the quality and quantity of bone affect the survival time of implants?

Characteristics of HA Coating

There has been much debate about when to use metallic or HA-coated implants. As mentioned earlier, HA-coated implants stimulate bone growth and have been shown to have a greater percentage of bone-to-implant integration. However, there are also some studies showing that HA is a very unstable implant material under some conditions (inflammation, infections, micromotion) and can prove detrimental to bone and tissues in the long term. As one example, [Gottlander and Albrektsson \(1991\)](#) examined the bone-to-implant contact area both at 6 weeks and 12 months for HA-coated and CPTi implants. They concluded that the bone-to-implant contact area at 6 weeks was 65% for HA and 59% for Ti. However, at 12 months, Ti exhibited a 75% contact area versus 53% for HA. Some contend that the interactions of HA with bone are biologically unstable because of this interface exchange. As mentioned earlier, HA can also be subjected to dissolution, and higher crystallinity must be maintained to minimize this occurrence. Unfortunately, some amount of amorphous biomaterial is often present during plasma-spray processing of the coating, and this substance is susceptible to dissolution. The long-term stability of HA-coated implants is still very controversial. Although the bond between HA and bone is considered to be strong, the mechanical stability of the interface between the coating and the metallic substrate may be unstable under some conditions.

Some studies have shown that the survival rate of HA-coated implants is initially higher than that for titanium plasma-sprayed implants, but in one study, the survival rate significantly decreased after 4 years. Failures were associated with inflammation of the surrounding tissues, with delamination and exfoliation of the implant. Some implants were retrieved before failure; these revealed partial loss of the HA coating, with flattening and thinning in some areas and an increase in local Cl and Mg ions. The implications of these factors relative to clinical implant failure remain unknown. Another concern is the adherence of microorganisms to the HA surface. A study of failed titanium plasma-sprayed and HA-coated implants revealed a colonization of coccoid and rod-shaped bacteria on HA implants, possibly as a result of the bioreactivity of HA. The roughened surface of the HA implants can also contribute to plaque growth, peri-implantitis, and dissolution once the coating is exposed. This can decrease the chance of long-term survival.

Another study compared the torsional strength of CPTi, Ti-6Al-4V, and HA-coated implants ankylosed in bone. The torque of separating for a period of up to 4 months ranged from 74 N-cm for the uncoated implants to 186 N-cm (HA-coated implants). These torsion-resistance values reflect the rotational shear resistance of the implant. Thus HA-coated implant surfaces in this circumstance provided greater implant–bone interface area,



• **Figure 12-14** Four qualities of bone.

higher shear tolerance, and higher torsional strengths in areas where a sinus lift procedure had been conducted.

HA Coating and Bone Quality

As previously stated, the type of bone in which the implant will be placed is of critical importance. Bone for implantation has been classified into four types: type I consists of mostly homogeneous compact bone, type II consists of a thick layer of compact bone surrounding a core of dense trabecular bone, type III is a thin layer of cortical bone surrounding a core of dense trabecular bone, and type IV is composed of a thin layer of cortical bone with a core of low-density trabecular bone (Figure 12-14). Type IV bone is by far the most compromised bone environment for implant stability because of its inadequate quality and quantity.

In spite of all its possible disadvantages, hydroxyapatite has multiple indications for implant applications. Studies reporting on the biological response to both the coated and uncoated implants suggest that HA-coated implants were interfaced intimately with bone and that the mineralized matrix extended into the microporosity of the HA coating. Numerous osteocytes were found along the periphery of HA-coated implants, which indicates that these implants are a better option for areas of poor bone quality, such as the maxilla. In one study, Brånemark-type titanium implants were evaluated in type IV bone, and a survival rate of 63% was found for mandibular implants and 56% for maxillary implants. These values are lower than the survival rates of 90% or more when these implants were placed in type I and II bone.

Another study compared the survival rates of titanium screw-type implants and HA-coated cylinders in type IV bone. At 36 months, Ti implants had a survival rate of 78% compared with 98% for HA implants. At 48 months, this survival rate fell to 75% for the metal implants. In a follow-up study, titanium screws exhibited a 91% 3-year survival rate and 89% for a 7-year period in type IV maxillary bone. These rates can be compared with a survival level of 95% for HA implants during a 7-year period. All of these studies indicate that HA-coated implants have a greater survival rate in type IV bone. Therefore many recommend the use of HA-coated implants in areas of poor or less-than-ideal bone as sites for implant placement. The bone height available for implant placement is also a factor in considering which type of implant to use. A 5-year study revealed a 70% failure rate in bone for titanium screws with an implant length of 8 mm. HA-coated screws of the same length had only a 4% failure rate over this period. There was no significant difference in the failure rates between the two types of implants when the length of the screws was increased to 12 mm.

Another indication for HA-coated implants was their use in fresh extraction sites, owing to the initial stability afforded by

these types of implants. Implant placement can sometimes be performed immediately after an extraction. Initial stability has been reported to be difficult to obtain in some of these cases, and this could lead to implant loss. A comparison of the survival rate of HA-coated implants, metallic implants, and hollow basket implants was made after 7 years of immediate implant placement. Survival rates of 95%, 90%, and 82% were found, respectively. The implant–bone interface contact area was also shown to be 62% for HA-coated implants and 29% for metallic implants after 28 days of placement.

Further advances in the field of dental surgery have allowed placement of implants in areas where bone was not normally present or had been lost. Maxillary and nasal sinus lifts are commonplace in partially dentate individuals who need an implant-based reconstruction. Bone grafts have enabled the placement of a sinus lift in posterior areas where bone is deficient. Unfortunately, the quality of bone produced from these bone grafts is of lower quality, and an implant needs a substantial implant–bone contact area for function. Most of these implant sites oppose fully dentate arches, which normally exert a higher amount of masticatory force. Thus initial stability, enhanced bone integration, and higher strength are important implant properties for these locations. Studies have revealed that HA-coated implants exhibited a push shear bond strength of 7 MPa versus 10 MPa for titanium metallic implants after a period of 10 weeks. After 32 weeks, HA-coated implants continued to have shear strengths five times greater than those of metallic surface implants.

The controversy that the resorption of HA coating over time could compromise long-term implant survival was examined in a meta-analytic review by Lee et al. (2000) that reported the outcomes of HA-coated implants in human clinical trials. This review suggests that the survival rates are similar for both and that the HA coating did not compromise the long-term survival of these implants. Indications from reviews supporting the selection of HA-coated implants over titanium- or metal-surfaced implants include (1) the need for greater bone–implant interface contact area, (2) the ability to place the implant in type IV bone, (3) fresh extraction sites, and (4) newly grafted sites. It has also been shown that the advantages of HA-coated implants are mainly short term in nature and are related to the initial stability of the implant, which most often determines its prerestorative success or failure.

CRITICAL QUESTION

Several types of biocompatibility test data may be useful in selecting an appropriate implant. What is the principal factor on the basis of which an implant material should be selected as suitable or unsuitable for osseointegration?

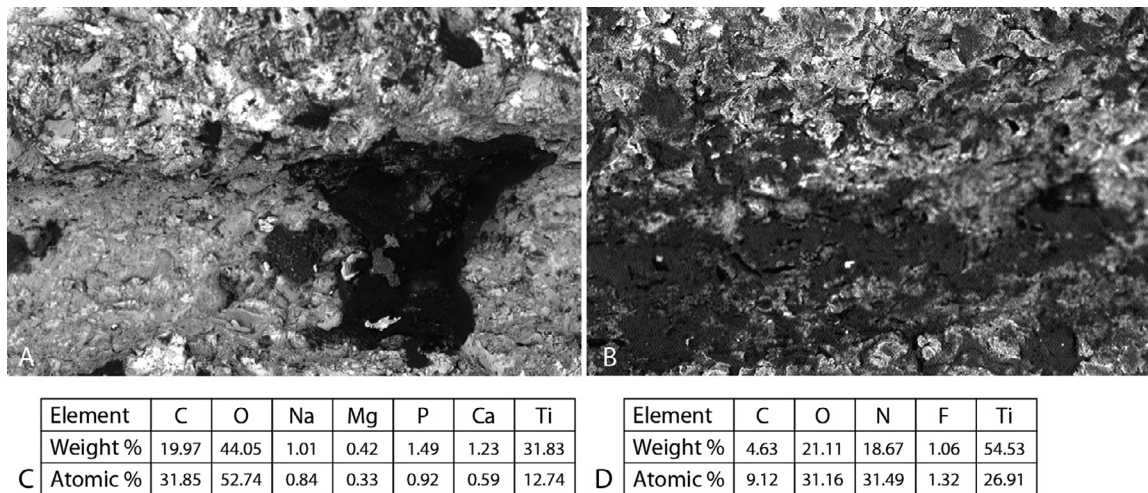
Biocompatibility of Implants

The concept of biomaterial biocompatibility does not refer to total inertness but rather to the ability of a material to perform with an appropriate response in a specific application (Chapter 17, *Basic Concept of Biocompatibility*). Biocompatibility is affected by the intrinsic nature of the material, in addition to its design and construction. Therefore the state of biocompatibility may be specific to a particular situation or function. The American Dental Association outlines some acceptance guidelines for dental implants, including the following: (1) evaluation of

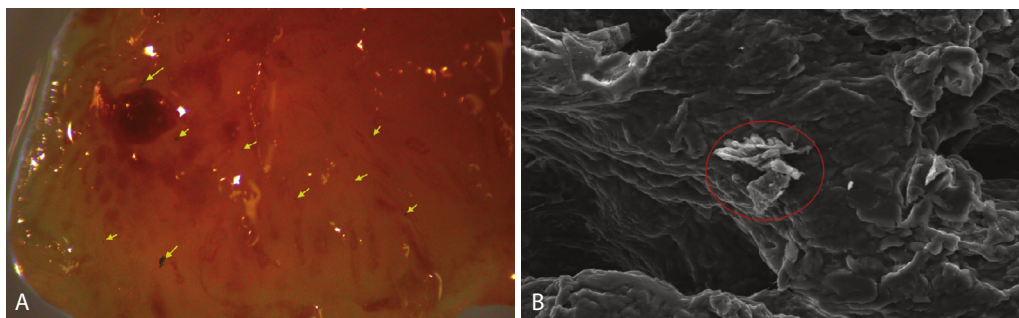
mechanical properties that ensure sufficient strength; (2) demonstration of ease of fabrication and sterilization potential without material degradation; (3) safety and biocompatibility evaluation, including cytotoxicity testing, and tissue interface characteristics; (4) freedom from defects; and (5) at least two independent longitudinal prospective clinical studies demonstrating efficacy.

The primary surface interactions between an implant material and the host take place at the surface of the implant within a region of approximately the size of one water molecule (about 0.275 nm). However, this does not mean that the implant–tissue interactions are isolated to this interface. Some studies have reported high titanium levels in both the spleen and lungs of rabbits immediately after surgery, but these concentrations were well within normal limits. In humans, Ti levels have been reported at 50 ppm, but they can reach levels of up to 200 ppm in tissues surrounding some titanium implants. At this level, tissue discoloration may be visible, but the material is still well tolerated by the body. Kasemo and Lausmaa (1991) demonstrated the dissolution of corrosion products into the bioliquid and adjacent tissues. Thus the outermost atomic layers of an implant are critical

regions associated with biochemical interactions of the implant–tissue interface. These reports emphasize the importance of process controls and a high degree of standardization and surface cleanliness in the production of implants. Most recently, there has been a focus on titanium corrosion (Figure 12-15) as a possible cause of peri-implantitis. As the titanium corrodes as a result of bacterial production of acidic toxins, the particles that lodge in the peri-implant tissues are believed to elicit an inflammatory response, which increases the progression of disease. To date, there is no predictable treatment for peri-implantitis disease. The recurrence rate after some form of therapy is usually 50%, and the disease progression eventually leads to loss of the implant and the prosthesis that the implant is supporting. Figure 12-16, A shows biopsied tissue from a peri-implant site demonstrating multiple titanium particles scattered throughout. Scanning electron microscopy (SEM) analysis was done to confirm this finding using x-ray diffraction analysis (Figure 12-16, B). Studies have also shown the presence of yellow nail syndrome, which results from systemic titanium leaching from titanium implants. This syndrome can manifest with symptoms such as yellow nails



• **Figure 12-15** Scanning electron microscopy (SEM) images of implant corrosion demonstrating breakdown of the surface with retrieved failed implant on the left (A) and reference implant on the right (B). Note increased roughened surfaces and increased corrosive landmarks on the failed implant. C, Corresponding EDAX analysis of failed implant (left image) showing decreased Ti and increased Mg and Na, indicative of corrosion. D, EDAX of reference implant (right image) for comparison.



• **Figure 12-16** A, Biopsied sample along diseased peri-implant site demonstrating presence of particles embedded in tissue (yellow arrows). B, Scanning electron microscopy (SEM) (×600) of biopsy sample showing one particle approximately 37 μm across (red circle) to be Ti by EDAX. (From Soler MD, Hsuv S-M, Fares C, et al: Titanium corrosion in peri-implantitis, *Materials (Basel)*. 2020;13(23):5488. doi:10.3390/ma13235488.)

and high titanium levels in the blood. Other manifestations include chronic sinusitis, bronchiectasis, and pleural effusions.

CRITICAL QUESTION

What are the important considerations for intraoral prosthesis design and material?

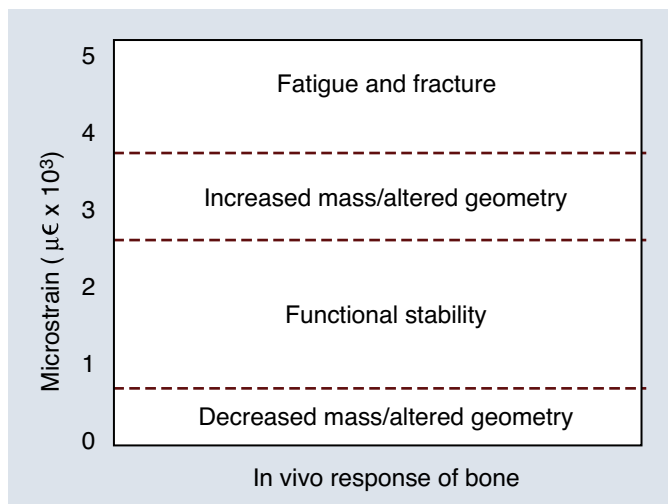
Biomechanics

The integration of bone with implants serves as the basis for the biomechanical analyses performed for dental implants. Close approximation of bone-integrated conditions with the surface of an implant permits the transfer of forces and site-specific stresses with elastic displacement of the bone and implant. The stresses that are generated are highly affected by four main considerations: (1) masticatory factors (frequency, bite force, and mandibular movements), (2) support for the prosthesis (implant supported, implant–tissue supported, implant–tooth supported), (3) the mechanical properties of the materials involved in the implant restoration (elastic modulus, yield strength, fracture strength, ductility, etc.), and (4) the design of the implant body and the associated intraoral prostheses. One of the most important variables affecting the close apposition of bone to the implant surface is the relative movement, or micromotion. Movement shortly after implantation prevents the formation of bone and encourages the formation of fibrous connective tissue around the implant surface. This collagen-rich connective tissue is known to be of lower modulus and strength. This is the reason that a delay of months for intraoral restoration has been recommended before loading after surgery. As mentioned previously, success has been reported with immediate loading of implants, depending on bone quality, patient selection, and short-term control of intraoral function. The key issue is control of implant-to-tissue micromotion during the initial healing of bone.

Numerous studies have defined the relationships for the response of bone to the types of biomechanical stresses and strains and their magnitudes. The results have been summarized as the “frost paradigm,” where microstrain magnitudes are correlated with bone conditions of disuse atrophy ($<500 \mu\epsilon$), normal function (500 to $1500 \mu\epsilon$), and microtrauma (more than $500 \mu\epsilon$). This concept is depicted schematically in Figure 12-17. This paradigm affords opportunities to evaluate implant and construct designs on a relative basis using finite-element models and analyses (FEM/FEA). Once again, this literature is well developed.

Two main types of loading conditions can occur at an implant site. These are represented by axial forces and bending moments caused by noncentric loading conditions. A bending moment can best be demonstrated by visualizing a cantilever beam design in which the maximum bending moment is located at the fixed base of support and is calculated as force (perpendicular to the beam) times the length of the lever arm. These bending moments become highly significant depending on the type and design of implant restoration planned.

Rangert (1989), Skalak (1983), and Brunski (1988) analyzed the theoretical effects of cantilever length, number of implants, arrangement of implants, and prosthesis design. Their models were based on the initial Brånemark hybrid prosthesis for the atrophic mandible (Figure 12-18). This type of restoration usually involves



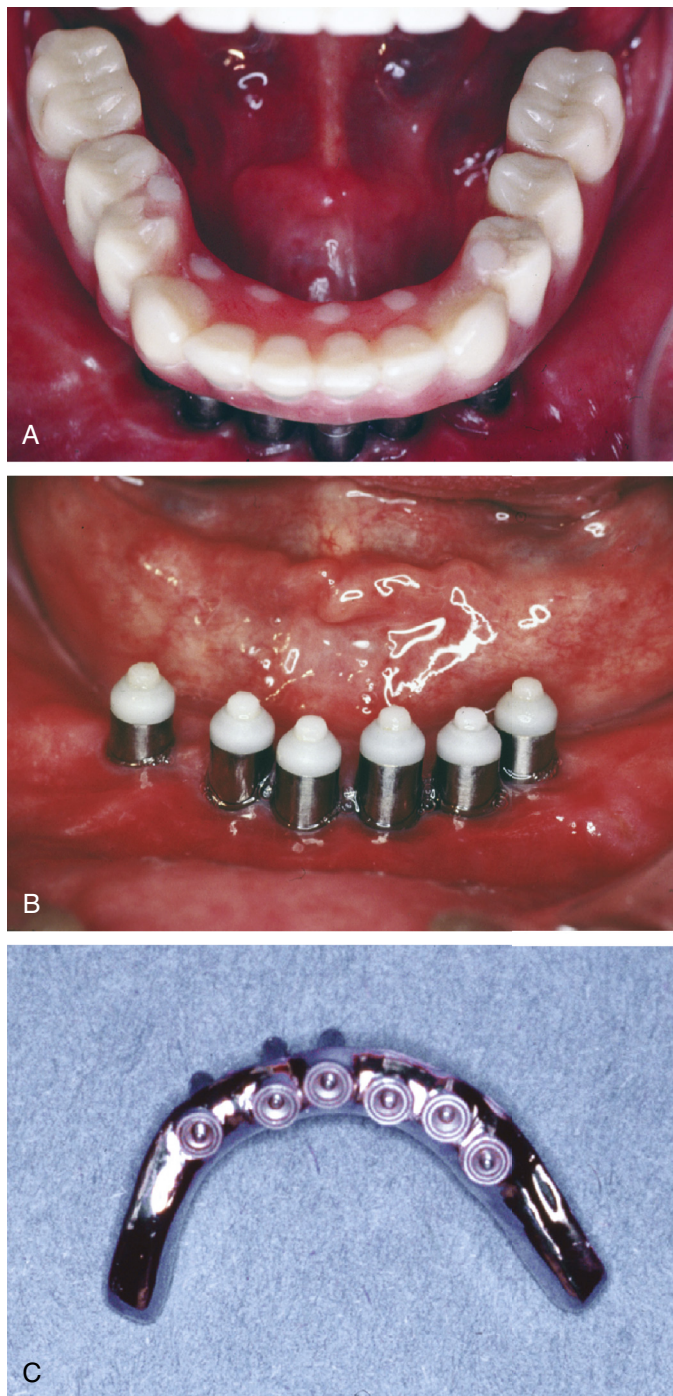
• Figure 12-17 Schematic diagram of Frost paradigm.

four to six implants confined to the area between the mental foramen of the mandible, with cantilevers extending from the most distal implant. These were restored with acrylic resin and denture teeth, which were attached to a metallic superstructure by the use of several types of attachment methods. The most significant aspect of these studies is the optimal ratio of the cantilever length to the interfixture distance.

When two or more implants are placed in a straight line, the bending moment will be distributed proportionately to the implants, provided that the intraoral prosthesis is designed to be sufficiently rigid. Placement of the implants in an offset manner has been suggested for more favorable positioning because it redistributes the implant loading. However, some recent studies have shown that tripodization of implants does not necessarily minimize stresses as much as the use of wider-diameter implants placed in a straight line. An increase in the anteroposterior placement of implants is also recommended to minimize the off-axis loading of the implant components. The load is greatest at the most distal implant when an anteriorly positioned cantilever prosthesis exists. Thus the distance between the most terminal abutment and the one adjacent to it should be increased to reduce the stress and strain induced within the most distal abutment.

Another important factor to consider is the fit of the prosthesis on the implant. An inaccurate fit will lead to a nonuniform distribution of load, with the unit closest to the load bearing most of the forces. For well-integrated implants, the weakest link in the early systems of Brånemark was the gold screw (also known as the *abutment screw*), which is regarded as the safety feature for these restorations. The external loads were transferred through the gold screw if an inaccurate fit or overload existed, and the screw would deform and fracture. These screws were fairly retrievable and were easy to replace. The ultimate tensile strength of the gold screw was designed to function within the normal ranges of occlusal force in the molar region.

Some guidelines include computing the anteroposterior span of all the implants and allowing a distance of 1.5 times any cantilever distance while limiting the maxilla to a maximal cantilever of 8 mm because of the limitations of bone quality. Any cantilever length over 7 mm causes a significant increase in microstrain within both the framework and bone. Therefore for any length



• **Figure 12-18** **A**, The original Brånemark hybrid prosthesis designed to accommodate severely atrophic mandibles. **B**, The hybrid prosthesis usually uses four to six implants. **C**, Corresponding superstructure that is screwed to the implants.

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- Albrektsson T, Zarb G, Worthington P, et al: The long-term efficacy of currently used dental implants: A review and proposed criteria of success, *Int J Oral Max Impl* 1:11–25, 1986.
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over 7 mm, ideal functional conditions should be considered, or the decision to proceed under less ideal conditions should be approached with extreme caution.

Another area of debate is the attachment of implants to natural teeth. The consensus seems to be that attaching implant intraoral prostheses to natural teeth should be limited and that having lone implants is a better restorative option. However, in cases using natural teeth in the restoration (e.g., when a low maxillary sinus position is present), there is disagreement as to whether or not this decreases the survival probability of the entire restoration. This issue stems from the different nature of attachments to bone between the implant and the tooth. The implant is integrated with bone (rigid), meaning that it has a direct connection with bone. On the other hand, a tooth is attached to bone through the periodontal ligament, which provides sensory functions to the tooth and also deforms in response to masticatory loads. Numerous reports have focused on these types of reconstructions; however, they should be approached with caution. Bone formation or resorption is determined by the tension or compression within the periodontal ligament. A concern associated with the attachment of an implant to a natural tooth is that the mobility of the tooth might minimize its load-sharing ability and overload the implant, understimulate the tooth, or cause a breakdown of the intraoral prosthesis. Several devices, such as the IMZ intramobile element, have been developed to allow the implant to accommodate the movement of the periodontal ligament. In any event, studies will continue to elucidate the effects of implant and natural tooth attachment on the probability of success. The results from most of the previous studies suggest that the attachment of natural teeth to implants does not compromise the prognosis of the prosthesis. Because these studies also confirm the overall excellent success rates of implant-supported prostheses, it is still recommended that this be the first approach for treatment.

Summary

The implant systems currently available are diverse. In 2020, there were hundreds of companies manufacturing many different systems. The implant biomaterials, for the most part, range from CPTi and titanium alloys to HA-coated devices. Manufacturers have developed individualized designs for their implants, which are now mostly root forms, and they are continually altering marketing strategies to highlight the features of each. Although most of the implant materials described in this chapter are believed to be biocompatible, the precise bone-bonding mechanisms are not fully characterized on a molecular level. When the mechanisms that ensure implant **bioacceptance** and structural stabilization are more fully understood, implant failures will become less, provided that implants are used properly and placed in sites for which they are indicated.

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13

Auxiliary Materials

OUTLINE

Classification of Impression Materials

Elastomeric Impression Materials

Hydrocolloids

Inelastic Impression Materials

Gypsum Products

Dental Waxes

KEY TERMS

IMPRESSION MATERIALS

Base paste (base putty) The component that forms the main three-dimensional structure of a final impression.

Catalyst paste (catalyst putty) A component of a polymerization reaction that decreases the energy required for the reaction and usually does not become part of the final product; however, the term *catalyst* has been used for the structural component of dental materials that initiates the polymerization reaction.

Colloid A solid, liquid, or gaseous substance made up of large molecules or masses of smaller molecules that remain in suspension in a surrounding continuous medium of different matter.

Elastomer Any of various polymers having the elastic properties of natural rubber.

Gel A network of fibrils forming a weak, slightly elastic brush-heap structure of hydrocolloid; also, the solid network structure of a crosslinked polymer.

Gelation The process of transforming a hydrocolloid from a sol to a gel.

Imbibition The displacement of one fluid by another immiscible fluid in a hydrocolloid. In the context of impression materials, imbibition is the uptake by agar or alginate when immersed in water.

Inelastic Incapable of sustaining significant elastic deformation without fracturing under stress.

Model A positive full-scale replica of teeth, soft tissues, and restored structures used as a diagnostic aid for the construction of orthodontic and prosthetic appliances; a facsimile used for display purposes.

Pseudoplastic A non-Newtonian behavior of fluids whose viscosity decreases under shear strain until it reaches a nearly constant value. Thus, the more rapidly pseudoplastic fluids are stirred or forced through a syringe, the less viscous (thinner) and more easily they flow.

Shear thinning The tendency for viscosity to decrease as the shearing rate increases (see *pseudoplastic* and *thixotropy*).

Static mixing A technique of transforming two paste-like materials (or fluids) into a homogeneous mixture without mechanical stirring; two streams of material are forced into a mixer cylinder, and the stationary elements in the mixer divide and recombine the feed materials and keep the material streams spiraling through the cylinder simultaneously.

Syneresis The expression of fluid onto the surface of gel structures.

Thixotropy The property of certain gels or fluids to become less viscous when sufficient energy in the form of impact force or vibration is applied; at rest, they require a specific duration to return to the previous viscous state. Both pseudoplasticity and thixotropy are shear-thinning processes; the difference is that changes in pseudoplastic viscosity do not exhibit the time dependency characteristic of thixotropy.

Viscoelastic/viscoelasticity The ability of a material to strain instantaneously like an elastic solid during rapid stretching or to resist shear flow and to strain linearly over time (like honey) when a stress is applied continuously.

GYPSUM PRODUCTS

Dental plaster (plaster of Paris) The beta form of calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$).

Dental stone The alpha form of calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$).

Hygroscopic setting expansion The expansion that occurs when gypsum or a gypsum-bonded investment sets while immersed in water (usually heated to approximately 38°C [100°F]).

Normal setting expansion The expansion that occurs when gypsum or a gypsum-bonded investment sets in ambient air.

WAXES

Baseplate wax Dental wax provided in sheet form to establish the initial arch form in the construction of complete dentures.

Bite wax A wax form used to record the occlusal surfaces of teeth as an aid in establishing maxillo-mandibular relationships.

Boxing wax A wax sheet form used as a border at the perimeter of an impression to provide an enclosed boundary for the base of the cast to be made from a poured material such as gypsum or resin.

Corrective wax (dental impression wax) A thermoplastic wax that is used to make a type of dental impression.

Dental wax (1) A low-molecular-weight ester of fatty acids derived from natural or synthetic components, such as petroleum derivatives, that soften to a plastic state at a relatively low temperature. (2) A mixture of two or more waxes and additives used as an aid for the production of gypsum casts, the production of nonmetallic denture bases, the registering of jaw relations, and laboratory work.

Flow Relative ability of wax to plastically deform when heated slightly above body temperature.

Inlay wax A specialized dental wax that can be applied to dies to form direct or indirect patterns for the lost wax technique, which is used for the casting of metals or hot pressing of ceramics.

Prosthetic devices and restorations are made to adapt to the anatomy of the oral tissue receiving the device. If the device is to be fabricated by the lost wax technique, a pattern with the exact dimensions of the device must be made with a material that is stable at room temperature but that can be removed by melting or burning out. The pattern usually is made of wax. To ensure close adaptation or fit for cementation of the fabricated device, the pattern must be fabricated on a model or die. A model (cast) or die can be made from gypsum products using an impression mold (or negative likeness) of a dental structure (Figure 13-1). Gypsum is a powder that, when mixed with water, becomes flowable and capable of being poured into an impression mold and capturing and reproducing the fine detail of the impression. Gypsum models are dimensionally stable during the entire process of pattern making and are resistant to scratching during pattern fabrication. To duplicate the anatomical form of the oral tissue, an impression material that is initially moldable is forced against the tissue and then sets. After removal, the impression should remain stable while models or dies are being made. These materials are required for making prostheses but do not become part of a final prosthesis. They are thus known as *auxiliary materials*. Impression materials, gypsum products, and waxes have multiple applications in addition to making prostheses. This chapter focuses on the use and relevant properties for general applications.

CRITICAL QUESTION

How are dental impression materials classified?



• **Figure 13-1** Impressions of dentate (left) and edentulous arches (right) with the resulting respective gypsum casts.

Refractory Capable of sustaining exposure to a high temperature without significant degradation.

Sprue The mold channel through which molten metal or ceramic flows into a mold cavity.

Sticky wax A type of dental wax that exhibits high adhesion to dry, clean surfaces when heated to a plastic condition.

Classification of Impression Materials

To produce accurate replicas of intra- and extraoral tissues, the impression materials should be (1) sufficiently fluid to adapt to the oral tissues, (2) viscous enough to be contained in a tray, (3) able to transform (set) into a rubbery or rigid solid in the mouth in a reasonable time (<7 minutes), (4) resistant to distortion or tearing when removed from the mouth, (5) dimensionally stable long enough to allow one or more casts to be poured, (6) biocompatible, and (7) cost-effective in terms of the required processing time and the expense of the materials and associated processing equipment.

By their composition, the impression materials are divided into three major groups: nonaqueous **elastomers**, hydrocolloids, and inelastic materials. Elastomers include polysulfide, condensation and addition silicone, and polyether. Hydrocolloids are alginate and agar. Inelastic materials comprise impression compound, plaster of Paris, and zinc oxide–eugenol (ZOE).

They are also classified by mechanism of setting, mechanical properties, and clinical applications. The setting mechanisms of impression materials can be reversible and irreversible. Reversible materials, such as agar and impression compound, soften upon heating and retain the shape when cooled in the oral cavity, with no chemical changes taking place. Irreversible materials imply that chemical reactions have occurred during impression making. The set impression materials can be inelastic (rigid) or elastic. Set rigid materials are highly resistant to flexure but fracture when deformed. They include ZOE impression paste, impression plaster, and impression compound. The term *elastic* in impression materials means that the material can be flexed easily without fracture and returns to its original form when unstressed. Hydrocolloids and elastomers fall into this category. The ability of elastic impression materials to rebound after removal from the mouth makes them suitable for reproducing both the hard and soft structures of the mouth, including the undercuts and interproximal spaces. **Inelastic** impression materials, such as ZOE and plaster, are ideal for making impressions of edentulous jaw structures or soft tissue because they do not compress the tissue during seating of the impression tray. Impression compound is often used to make trays for the construction of full dentures. Table 13-1 shows the classification based on the setting mechanism and mechanical characteristics.

Environmental conditions and the type of tissue dictate the choice of materials, the quality of the impression, and the quality of the cast. The next three sections discuss the unique properties of three categories of impression materials by composition and describe how they affect the quality of the impressions and the casts.

Elastomeric Impression Materials

Elastomeric impression materials are crosslinked polymers when set that can be stretched and yet rapidly recover to their original dimensions when stress is released. Chemically, there are three elastomers based on polysulfide, silicone (polysiloxane), and polyether. A background covering the underlying fundamentals of polymeric materials is presented in Chapter 2, **Polymers**.

TABLE 13-1 Classification of Dental Impression Materials

Setting Mechanism	MECHANICAL CHARACTERISTICS	
	Inelastic	Elastic
Chemical reaction (irreversible)	Plaster of Paris Zinc oxide–eugenol	Alginate Polysulfide Polyether Condensation silicone Addition silicone
Thermally induced physical reaction (reversible)	Impression compound	Agar

Chemistry of Elastomeric Impression Materials

Elastomeric impression materials are supplied in two components, a base and a catalyst (or accelerator), that are mixed before making impressions. The term *catalyst* or *accelerator* used here may be a misnomer with certain material systems. *Reactor* is a more appropriate term for the polysulfide and condensation silicone because they participate in the reaction. In the case of polyether, the catalyst contains initiators. The materials are often formulated in several consistencies, including extra low, low, medium, heavy, and putty, in increasing order of filler content. Extra-low and putty forms are available only for condensation and addition silicones. Polysulfide is provided only in light-body and heavy-body consistencies. Pigments are added to give each material a distinct color. As a group of impression materials, elastomers are classified by consistency measured immediately after complete mixing as type 0: putty, type 1: heavy-bodied, type 2: medium-bodied, and type 3: light-bodied (International Organization of Standard ISO 4823:2015).

Polysulfide

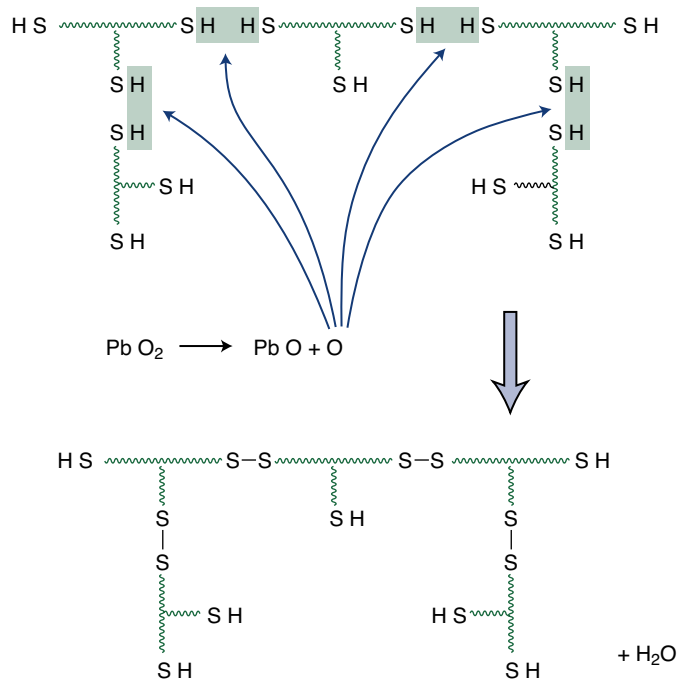
The **base paste** contains a liquid prepolymer with multifunctional mercaptan (–SH) groups, a suitable filler to provide the consistency for mixing and the required strength when set, a plasticizer to confer the appropriate viscosity for workability of the paste, and a small quantity of sulfur (~0.5%) to accelerate the reaction. The **catalyst paste** contains lead dioxide, filler, and plasticizer, as in the base paste, and oleic or stearic acid as a retarder to control the rate of the setting reaction. Each paste is supplied in a dispensing tube with appropriately sized bore diameters at the tip so that equal lengths of each paste are extruded from each tube to provide the correct ratio of base to crosslinking agent.

The reaction starts as soon as mixing begins, and a resilient network has started to form (Figure 13-2). During the final set, a material of adequate elasticity and strength is formed so that the impression can be removed past undercuts quite readily. Elevated temperature and humid conditions will accelerate the setting of polysulfide impression material. The reaction yields water as a by-product. Loss of water from the set material has a significant effect on the dimensional stability of the impression.

Condensation Silicone

The materials are supplied as a base paste and a liquid catalyst, a two-paste system, or a two-putty system. The putty can be used as the tray material in conjunction with a low-viscosity silicone, which is referred to as the *putty-wash technique*.

The base paste consists of α - ω -hydroxyl-terminated polydimethyl siloxane (Figure 13-3). The curing of this material



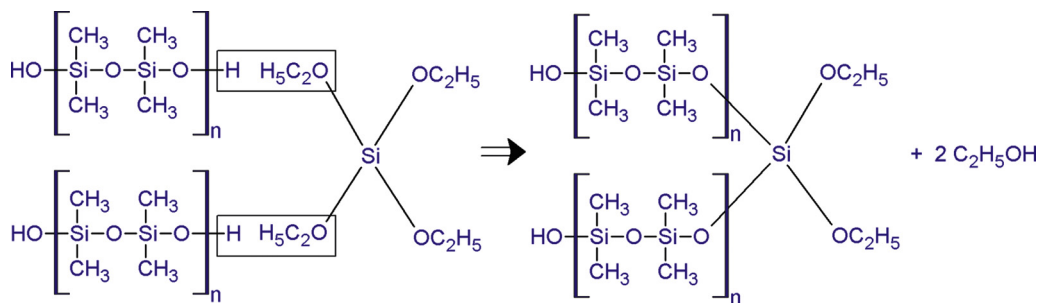
• **Figure 13-2** Polymerization of polysulfide impression material. SH groups interact with oxygen released from lead dioxide (left). Completion of the condensation reaction results in water as a by-product (right). Pendant –SH is for crosslinking, and terminal –SH is for chain lengthening of the polymer.

involves a reaction of tri- and tetra-functional alkyl silicates in the presence of stannous octoate as a catalyst. The material sets by condensation reaction between terminal groups of the silicone polymers and the alkyl silicate to form a three-dimensional network (Figure 13-3). Ethyl alcohol is a by-product of the condensation reaction that evaporates, and the evaporation accounts for much of the contraction that occurs during setting.

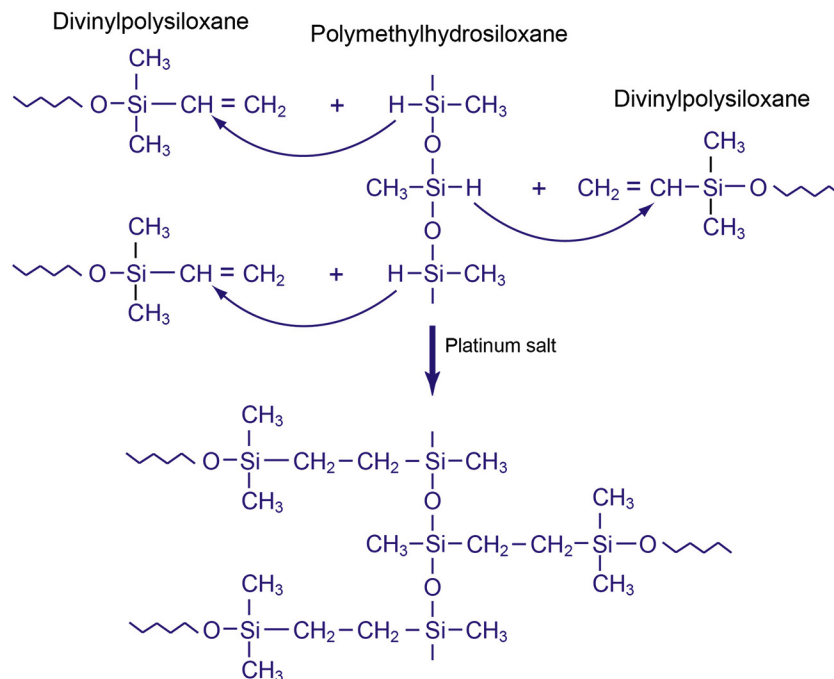
Addition Silicone

This material is often called a *polyvinyl siloxane* (PVS) or *vinyl polysiloxane* (VPS) impression material. The base paste contains polymethylhydrosiloxane and other siloxane prepolymers. The catalyst paste contains divinylpolysiloxane and a platinum salt. Both pastes contain fillers. The addition silicone is based on addition polymerization between divinylpolysiloxane and polymethylhydrosiloxane with a platinum salt as the catalyst (Figure 13-4). No reaction by-products are formed if the correct proportions of base and catalyst pastes are used and there are no impurities. However, the residual polymethylhydrosiloxane in the material can lead to a secondary reaction with each other or with moisture, producing hydrogen gas. Technically, hydrogen gas is a reaction by-product that does not affect the dimensional stability of the impression. Nonetheless, the hydrogen gas evolved can result in pinpoint voids in the gypsum casts poured soon after the removal of the impression from the mouth. A noble metal, such as palladium, can be added as a scavenger for the released hydrogen gas. The impression should be left overnight if epoxy is used for pouring models.

Sulfur contamination from natural latex gloves inhibits the setting of addition silicone. Some vinyl gloves may have the same effect because of the sulfur-containing stabilizer used in the manufacturing process. The contamination is so pervasive that touching the tooth with latex gloves before seating the impression can inhibit the setting of the critical surface next to the tooth.



• **Figure 13-3** Condensation polymerization of α - ω -hydroxy-terminated poly (dimethyl siloxane) with tetraethyl orthosilicate in the presence of stannous octoate (catalyst). The reaction results in the release of ethanol molecules.



• **Figure 13-4** Polymerization of addition silicone. Hydrogen atoms along the backbone structure of the vinyl silicone chain move to the vinyl groups during addition polymerization (*top*). Final structure after the platinum salt has initiated the addition polymerization reaction (*bottom*). The zigzag line at the other end of divinylpolysiloxane represents repeating units of dimethylsiloxane with a vinyl terminal.

Medium-body addition silicone has also been formulated for making impressions for diagnostic purposes, as a substitute for alginate impression material, an irreversible hydrocolloid to be discussed later. The advantage of these so-called *alginate substitutes* is the ability to make multiple, accurate diagnostic casts from one impression. Laboratory studies have reported that they exhibited better detail reproduction and less variability in linear dimensional change than alginates.

Polyether

There are two types of polyether impression materials. The first is based on the ring-opening polymerization of aziridine rings, which are at the end of branched polyether molecules (Figure 13-5). The main chain is probably a copolymer of ethylene oxide and tetrahydrofuran. Crosslinking and setting are promoted by an initiator and an aromatic sulfonate ester, where R is an alkyl group. This produces crosslinking by cationic polymerization via the imine end groups. The base paste contains the polyether prepolymer, colloidal silica as filler, and a plasticizer such as glycol ether or phthalate. The accelerator paste contains an alkyl-aromatic sulfonate in addition to the filler and plas-

ticizer. The ether-dominated polymer backbones make this group of materials the most hydrophilic of all elastomeric impression materials.

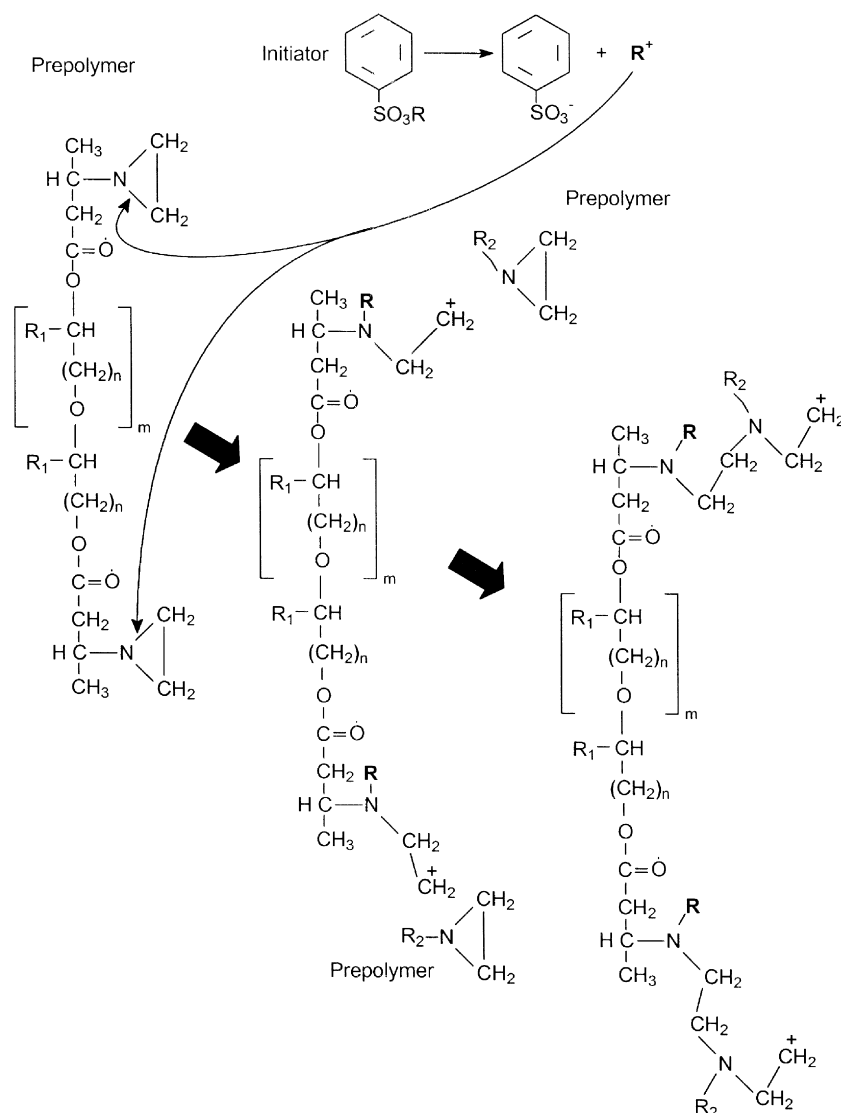
CRITICAL QUESTION

What are the steps needed to produce casts and dies for prosthetic procedures?

The second type is based on an acid-catalyzed condensation polymerization (Figure 13-3) of polyether prepolymer with alkoxysilane terminal groups. The mechanism is like that observed in condensation silicones having low-molecular-weight alcohols as by-products. This material is often called a *hybrid*. Because the ether linkages constitute the main component of the polymer chains, these materials behave very much like the first type of polyether impression material.

Making Impressions With Elastomeric Materials

The use of elastomeric impression material to fabricate gypsum models, casts, and dies involves six major steps: (1) preparing a tray, (2) managing tissue, (3) preparing the material, (4) making



• **Figure 13-5** Ring-opening polymerization of polyether. The initiator, aromatic sulfonate ester, dissociates (top) and forms alkyl cations that bind the nitrogen atoms of the aziridine ring terminals of the prepolymer (left). The arrows indicate binding between the cations (R^+) with the nitrogen atoms. This action opens the ring, and the reacted prepolymer (center) now has two charged ethylene imine terminals ($-NR-CH_2-C^+H_2$), which can react with the nitrogen atoms of adjacent unreacted prepolymers, shown as the R_2 -aziridine ring. This chain-propagation polymerization reaction yields a larger molecule (right), which continues growing by binding with the aziridine rings of additional unreacted prepolymers. The polymerization reaction terminates when the growing chain combines with a counterion.

an impression, (5) removing the impression, and (6) preparing for stone casts and dies.

Impression Trays

The use of a custom tray (Figure 13-6, left) requires less impression material than a stock tray to make impressions, thus minimizing dimensional changes attributable to the materials. A custom tray allows a uniform distribution of impression material between the tray and the tissue, which also improves accuracy. This is especially true for polysulfide impression material. The use of custom trays for polyether and addition silicone impressions is not critical because these materials are stiffer and have less polymerization shrinkage than polysulfide. In addition, disposable stock trays (Figure 13-6, right) work satisfactorily. Note that the use of less material in a custom tray reduces the compressibility of the



• **Figure 13-6** Impression trays. Custom tray (left) and stock tray (right).

impression, which can make removal of the impression tray more difficult. When severe undercuts are present, the use of a custom tray should be avoided. The stock tray should be rigid, thereby minimizing flexure of the tray during impression removal. Prior to making an impression, a uniform thickness of tray adhesive is applied on the tray surface, extending over its edge, and allowed to dry (through evaporation of solvent). Tray adhesives are not interchangeable among different types of materials.

Tissue Management

The margins of tooth preparations for fixed prostheses often extend to or below the free margin of the gingiva. To ensure access for the tooth preparation and for making the impression, displacing the gingival tissues is necessary to control gingival hemorrhage and sulcular fluids from distorting the margins of the crown preparation. Among the most popular methods of gingival displacement is the use of gingival retraction cord. An electrosurgical unit or a soft tissue laser can also be used.

Placing a retraction cord displaces the gingival tissue laterally away from the margin of the preparation. One or two gingival retraction cords are placed under the margin around the tooth for at least 5 minutes before making impressions. The double-cord technique is used when the margin is very close to the gingival attachment. A fine cord is placed at the base of the crevice to

facilitate moisture control, with a larger cord placed on top of the first and near the coronal extent to displace the gingiva laterally. The outermost cord is removed, leaving the fine cord within the crevice while the impression is made. A single cord is sufficient to deflect the soft tissue around the margin when the preparation margin is at or slightly above the gingival crest.

Retraction cords may be impregnated with a hemostatic agent by dipping the cord in a hemostatic solution prior to placement. These agents can have unintended side effects and should be used with caution. For example, epinephrine, which is used widely, is of concern in patients with cardiovascular disease. In addition, agents with a low pH can remove the smear layer and superficial dentin apical to the margins of the preparation, possibly leading to postoperative sensitivity of some teeth.

CRITICAL QUESTION

How does static mixing achieve a uniform mixture? What is the main difference between static mixing and dynamic mixing?

Manipulation of Impression Materials

Currently, elastomeric impression materials are offered for three modes of mixing: hand mixing, **static mixing**, and dynamic mechanical mixing (Figure 13-7).



• **Figure 13-7** Mixing systems. **A**, Hand mixing. Two equal lengths of the material are dispensed on the mixing pad with the mixing spatula. **B**, Static mixing. When the trigger is pulled, the plunger is driven forward (to the left) so that the base and catalyst pastes are forced from the cartridge into the mixing tip (*extreme left*). The pastes pass through the bore and exit the nozzle as a uniform mixed paste. Four different sizes of mixing tips are shown; the more viscous the material, the larger is the mixing tip that should be used. Syringe tips can be fit to the nozzle to deliver the mixed paste directly to the prepared teeth. **C**, Static mixing syringe. These syringes fit the cartridge, such as the mixing tips shown in (**B**). The base and catalyst are first injected into the respective barrel. A plunger then forces the material through a smaller static mixing tip. It can deliver the light-body material directly onto the abutment(s). **D**, Dynamic mechanical mixing. The motor-driving mechanism forces the material into the mixing tip and makes the impeller (*insert*) inside the tip rotate. The function of the impeller is only to mix the material.

Hand Mixing

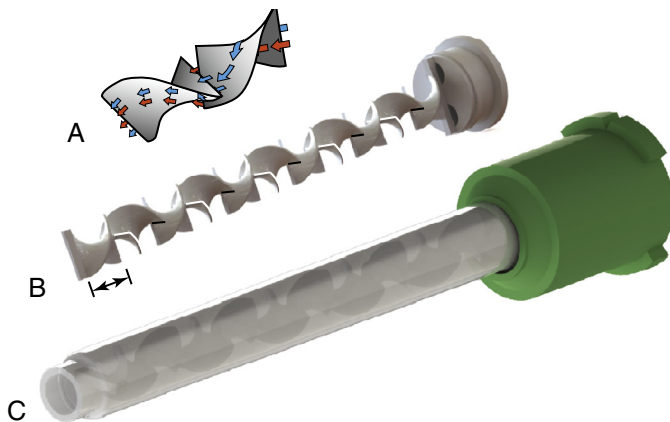
The user dispenses the same lengths of materials onto a mixing pad (Figure 13-7, A). The catalyst paste is first collected on a stainless-steel spatula and then spread over the base paste. The mixture is spread over the mixing pad. The mass is then scraped up with the spatula blade and spread uniformly back and forth on the mixing pad. This process continues until the mixed paste is uniform in color, with no streaks of the base or catalyst appearing in the mixture. If one of the components is in liquid form, such as the catalyst for condensation silicones, a length of the base is dispensed from the tube onto a graduated mixing pad, and drops of the liquid catalyst corresponding to the length of the base are added.

The two-putty systems available for condensation and addition silicone are dispensed by volume using an equal number of scoops of each material. The best mixing technique is to knead the material with one's gloved fingers until a uniform color is obtained.

Static Mixing

This technique transforms two flowable (or paste-like) materials into a homogeneous mixture without mechanical mixing. The device comprises a gun for pushing materials in a two-cylinder cartridge (base and catalyst), along with a mixing tip (Figure 13-7, B). The mixing tip is made of helical mixer elements in a cylindrical housing (Figure 13-8). The mixer elements are a series of alternating right- and left-turn 180° helixes positioned so that the leading edge of one element is perpendicular to the trailing edge of the other one (Figure 13-8, B).

The base and catalyst are pressed from the cartridge into the mixing tip as one stream of a two-layer material. The leading edge of the first element splits the material entering the mixer into two streams. The streams that flow on either side of the helix will make a 180° turn (Figure 13-8, A) when they reach the second element. Both streams are split by the leading edge of the second element and become two streams of four-layer material (two layers from each original stream)



• **Figure 13-8** Design of a static mixing tip. **A**, Mechanism of mixing in a two-element model. The two-element model shows that the materials injected into a left-turn helix are immediately split into two streams. Both streams make a 180° counterclockwise turn when they reach the leading edge of the next element, a right-turn helix. Each stream is split as it enters the new element. Two new streams, made of combining two substreams, one from each original stream, now make a 180° clockwise turn when they reach the trailing edge of the element. When there is a third element present, each substream will be split again, and the total number of substreams will be eight (2^3). **B**, Mixer elements with 11 helixes. The double-headed arrow delineates the size of one element. The appearance of a size difference between neighboring elements is caused by the orientation. **C**, Mixing tip with encased mixer elements. (Courtesy Dr. Karl-Johan Söderholm.)

entering the third element. This process is known as *flow division*. Even if there is no intermixing between layers as they merge to a new stream, there will be 2^n layers in either stream as they come out of the n th element. For a mixing tip with 11 elements, the stream that exits the mixing tip will have a 2048-striation structure, which is practically a uniformly mixed stream of material. In addition, as the materials make turns along the helix, the rotational circulation causes a radial mixing of the materials. Thus mixing between layers occurs before the subsequent flow division that further increases the uniformity of the mixture. Because there is no mechanical mixing, porosity caused by mixing with air is avoided.

The mixed impression material is injected directly into the adhesive-coated tray or, if the “syringe tip” is in place, onto the prepared teeth. One can also use an intraoral syringe (Figure 13-7, C) to apply light-body material onto prepared teeth. One precaution that should be taken is to make sure that the openings of the cartridges that dispense the pastes remain unclogged. Problems can be avoided if one expresses a small amount of material from the cartridge before attaching the mixing tip and discards the first centimeter of mixture that emerges from the mixing tip. This process is called *bleeding*. This type of device has also been adapted to mix and dispense acrylic-based materials for fabricating temporary crown and bridge, and luting cements that are used for luting prostheses (Chapter 7, Clinical Manipulation and Evaluation).

Dynamic Mechanical Mixing

The device shown in Figure 13-7, D uses a motor to drive parallel plungers, forcing the materials into a mixing tip and out into an impression tray or syringe; meanwhile, the motor-driven impeller, which is inside the mixing tip, mixes the materials as they are extruded through the tip. The function of the impeller is only to mix the materials as they are passing through; it does not propel the material. The materials are supplied in collapsible plastic bags housed in a cartridge. The amount of material retained in the mixing tip is slightly greater than that used in static mixing. In using this device, thorough mixing of higher-viscosity materials can be achieved with little effort. Both polyether and addition silicone impression materials of various viscosities are available with this dispensing system.

CRITICAL QUESTION

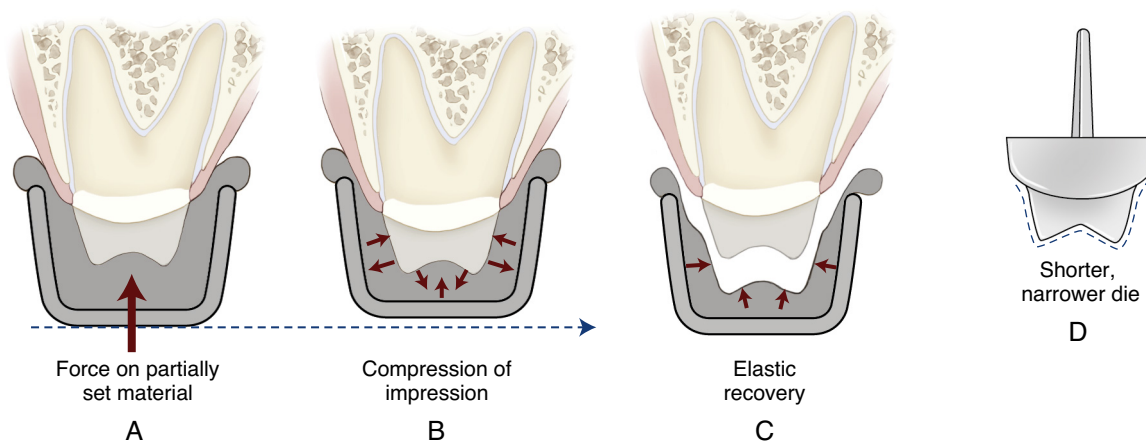
How does each impression-making technique take advantage of the unique properties of the impression materials?

Techniques of Making Impressions

Elastomeric impression materials are typically supplied in several viscosities to accommodate the different techniques for impression making. Three techniques for making impressions are discussed in this section.

Multiple-Mix Technique

A syringe material (light body) and a tray material (heavy body) are used in this technique. When they are hand mixed, they are mixed simultaneously, each by a different person because one must load the syringe with the light-body material. With mechanical devices, the materials can be mixed as needed by one individual. The lighter material is dispensed from the filled syringe or directly from a static mixing gun within and around the tooth preparation. The filled tray is then inserted in the mouth and seated over the syringe material. The tray material will force the syringe material to adapt to the prepared tissues. The two materials should bond together upon setting. If either material has progressed past



• **Figure 13-9** Effect of seating-tray material that has passed its working time and developed some elasticity. **A**, Impression tray containing elastomeric impression material is seated too late as elasticity starts to develop. **B**, Increased seating pressure is applied to overcome the stiffness of impression material. **C**, Distortion develops during the recovery of excessive elastic deformation (springback). **D**, The die produced in the inaccurate impression is too narrow and too short.

the working time when brought together, the bond between them will be compromised. If a partially set material is seated, the material will be compressed elastically. Once removed from the mouth, the impression will “spring back” or relax, and the dies made from this impression will be too narrow and too short, as illustrated in Figure 13-9.

In rare cases a clinician may attempt to repair an impression that has small defects or that lacks sufficient detail. This is usually performed by cutting away the interproximal and gingival areas of the impression. Reseating the tray precisely will be difficult even with proper relief of the initial impression. Entrapment of a minute fragment of impression material or debris will eliminate any chance of a successful repair. The impression material’s surface must be roughened to ensure that the new material bonds to the set impression. The safest method is to make a new impression when bubbles or similar defects are detected in critical areas.

Monophase Technique

Medium-body polyether and addition silicone are often used for the monophase or single-viscosity technique. The procedure is like that of the multiple-mix technique except that only one mixture is made, and part of the material is placed in the tray, and another portion is placed in the syringe for injection in the cavity preparation, prepared teeth, or soft tissue. The success of this technique depends on the pseudoplastic (**shear-thinning**) properties of the materials. When a medium-viscosity material is forced through the syringe tip, the viscosity is reduced, facilitating material adaptation to the preparation. Meanwhile, the material in the tray retains a medium viscosity, and when seated, the tray material can force the syringe material to flow past critical areas of the tooth preparation. Table 13-2 shows the effect of shear rate and elapsed time on some monophase addition silicones.

CRITICAL QUESTION

What are the consequences of placing an impression material in the mouth after the working time has expired?

Putty-Wash Technique

The thick putty material is placed in a stock tray, and a preliminary impression is made. This procedure results in what is essentially an intraoral custom-made tray formed by the putty. Space for the light-body “wash” material is provided either by cutting away some of the “tray” putty or by using a thin polyethylene sheet as a spacer between the putty and the prepared teeth during preliminary impression making. A mixture of the thin-consistency wash material is placed into the putty impression and on the preparation; then the tray is reseated in the mouth to make the final impression.

Removal of the Impression

Under no circumstances should the impression be removed until the curing has progressed sufficiently to provide adequate elasticity. One method for determining the time of removal is to inject some of the syringe material onto a space that is not in the field of operation before inserting the impression tray. This material can be probed with a blunt instrument from time to time; when the material is firm and returns completely to the original contour, the impression is sufficiently elastic to be removed. Typically, the impression should be ready for removal within at least 10 minutes from the time of mixing, allowing 6 to 8 minutes for the impression to remain in the mouth. Manufacturers usually provide instructions as to the optimal time for removal after mixing.

The mechanics of removing the impression involve separation at the impression–tissue interface and stretching of the impression. The first step is to break the physical adhesion between the tissue and the impression; therefore an impression material, such as polyether, that wets the tissue well will require extra effort to break the adhesion (seal) for the removal. The second step is stretching the impression enough to pass under the height of contour of the hard tissue to remove the impression; therefore using a material of higher rigidity will require a greater force to stretch the impression to facilitate removal. Polysulfide has the lowest viscosity and ranks as the least stiff of the elastomeric impression materials of a similar consistency. This flexibility allows the set material to be easily removed from undercut areas and from the mouth with a minimum of stress.

TABLE 13-2 Viscosity ($\times 104$ cp) of Single-Phase Vinyl Polysiloxanes at 37 °C

Material	VISCOSITY AT 1 min		VISCOSITY AT 1.5 min	
	0.5 rpm	2.5 rpm	0.5 rpm	2.5 rpm
Baysilex (Miles)	122.1 (2.8) [†]	68.9 (2.5)	211.2 (14.7)	148.8 (1.2)
Green-Mouse (Parkell)	133.7 (8.9)	56.7 (2.9)	247.9 (14.9)	78.0 (2.8)
Hydrosil (Caulk)	194.2 (8.5)	129.4 (4.1)	398.1 (7.8)	153.5 [‡]
Imprint (3M)	106.5 (12.2)	79.7 (2.2)	245.1 (8.9)	146.2 (5.9)
Omnisil (Coe)	156.8 (11.5)	102.5 (1.9)	347.1 (5.2)	153.5 [‡]

[†]Numbers within parentheses represent the standard deviation of the mean.

[†]Value at 75 seconds after mixing.

[‡]Value at 77 seconds after mixing.

From Kim K-N, Craig RG, Koran A: Viscosity of monophase addition silicones as a function of shear rate, *J Prosthet Dent* 67:794, 1992.

In addition, all elastomeric impression materials are **viscoelastic**, and it is necessary to use a quick snap to minimize plastic deformation of the impression during the final step of the removal process. The phenomenon of viscoelastic behavior is discussed in subsequent sections.

Preparation of Stone Casts and Dies

The hydrophobic characteristics of silicone impression make pouring with gypsum products challenging because it increases the potential of forming voids in gypsum dies and casts. One can spray a thin layer of surfactant, also known as *debubblizer*, on the impression to improve the surface wettability for the stone mixture. A dilute solution of soap is also an effective surfactant. One can also select a hydrophilized addition silicone (discussed later) to make impressions. Pouring of a stone cast in a polyether or polysulfide impression does not require the aid of a surfactant.

The excellent dimensional stability of addition silicone and polyether impression materials makes the construction of two or three casts or dies from one impression possible. It is also possible to construct successive stone dies or casts from polysulfide impressions when duplicate stone dies are needed. It should be noted that each successive die will be less accurate than the first die constructed from the impression. One should wait before the next pour after the removal of the cast but not greater than 30 minutes. To minimize tearing and gross distortion after the first pour, the clinician should remove the excess gypsum-forming mass from undercut areas along the periphery of the tray. Be aware that the stiffness of the impression material makes it difficult to remove the stone cast from the impression. A weak stone cast may fracture during removal.

Properties of Elastomeric Impression Materials

The ability to make a cast or die that reproduces the surface details and precise shape of the original tissue depends on various properties of the impression material. In this section, the properties relevant to impression making with elastomers are described. The comparative properties of elastomeric impression materials are listed in Table 13-3.

CRITICAL QUESTION

Why is it not advisable to alter the base/catalyst (accelerator) ratio as a means of controlling working or setting time?

Working and Setting Times

The working time begins at the start of mixing and ends just before the elastic properties develop. The **setting time** is the time elapsed from the beginning of mixing until the material has enough strength to be removed from the mouth without distortion. Remember, however, that polymerization may continue for a considerable time after. An increase in temperature accelerates the rate of polymerization of all elastomeric impression materials; therefore the effect of temperature on working and setting time should be taken into consideration.

Altering the base/catalyst ratio will change the curing rate of these materials. Normally, having more base materials in the mixture tends to increase the working and setting times. Keep in mind that altering the base/catalyst ratio may not produce a predictable change in the polymerization rate.

CRITICAL QUESTION

Why is rapid seating of an impression tray not advisable for a pseudoplastic impression material?

Rheological Properties

Ideally, the impression material should flow freely and wet the tissue as it is being injected to achieve adaptation, then become immobilized immediately, which keeps the material from flowing away from the intended surface areas. The same property will facilitate spreading of heavy-body material on the impression tray and retain it in the tray. This phenomenon is called *shear thinning*, which was discussed in Chapter 3, *Rheology*. All elastomeric impression materials exhibit shear-thinning characteristics before setting.

There are two categories of shear thinning: **pseudoplasticity** and **thixotropy**. A pseudoplastic material displays decreasing viscosity with increasing shear stress and recovers its viscosity immediately upon termination of shear stress. A thixotropic material does not exhibit a reduction of viscosity until sufficient agitation (shear stress) is applied to overcome the yield stress of the material. After the termination of shear stress, it takes a specific time to regain its previous viscous state. The latter is important because it takes time for the impression material to adapt to the surface. Manufacturers often emphasize their materials as being thixotropic and also note that the materials exhibit no slump when injected on a vertical surface. They usually do not mention the duration of the time delay.

TABLE 13-3 Comparative Properties of Elastomeric Impression Materials

Property	Polysulfide	Condensation Silicone	Addition Silicone	Polyether
Working time (min)	4–7	2.5–4	2–4	3
Setting time (min)	7–10	6–8	4–6.5	6
Tear strength (N/m)	2500–7000	2300–2600	1500–4300	1800–4800
Percent contraction (at 24 h)	0.40–0.45	0.38–0.60	0.14–0.17	0.19–0.24
Contact angle between set material and water (°)	82	98	98/53*	49
Hydrogen gas evolution (Y/N)	N	N	Y†	N
Automatic mixing (Y/N)	N	N	Y	Y
Custom tray (Y/N)	Y	N	N	N
Unpleasant odor (Y/N)	Y	N	N	N
Multiple casts (Y/N)	N	N	Y	Y
Stiffness (value of 1 indicates greatest stiffness)‡	3	2 (1)	2 (1)	1 (2)
Distortion on removal (value of 1 indicates the greatest and 4 the least potential distortion)	1	2	4	3

N, no; Y, yes, Y/N, yes or no.

*The lower contact angle resulted from testing of a hydrophilized polyvinyl siloxane (PVS).

†A hydrogen absorber is often included to eliminate hydrogen gas evolution.

‡The numbers in the parentheses reflect the ranking when a soft formulation of polyether impression material is considered.

The benefit of thixotropy in impression making has been disputed because the time duration needed for the impression material to recover the necessary viscosity may be unacceptable. However, reports suggest that a thixotropic material should facilitate handling and make better impressions. One should be aware that these studies are often conducted with unmixed base and catalyst pastes. From the point of impression making, the viscosity of a uniformly mixed impression also increases with polymerization, regardless of the effect of thixotropy. Therefore the impact of thixotropy during impression making may not be critical. In addition, confirming the thixotropic nature of a material without reporting the time lag required before regaining the intrinsic viscosity is not meaningful.

CRITICAL QUESTION

How does the viscoelastic property of impression materials dictate the way an impression must be removed from a patient's mouth?

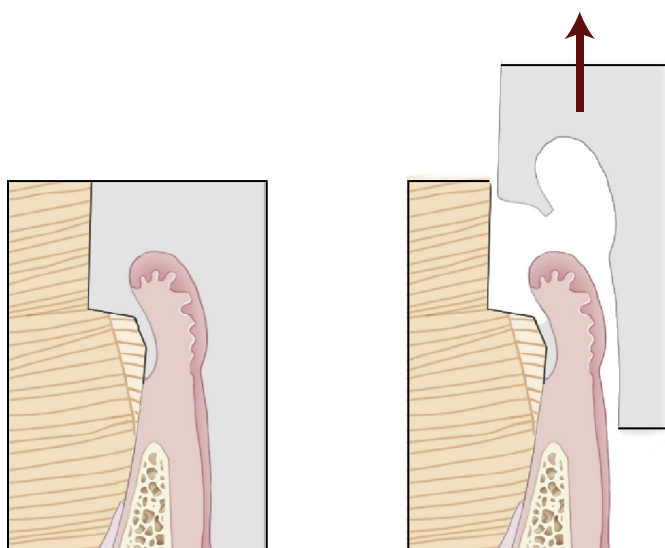
Elasticity and Viscoelasticity

An impression material sustains some deformation as it is removed from the mouth, but it must rebound to its preremoval dimensions to preserve the dimensions of the preparation. All elastomeric impression materials are viscoelastic and exhibit both viscous and elastic characteristics. Recall that viscous materials, such as honey, resist shear flow but continue to flow as long as stress is applied. Elastic materials strain (deform) when a stress is applied, but the strain does not increase with time if no additional stress is applied, and they immediately return to their original state once the stress is removed. Essentially, viscoelastic materials exhibit time-dependent strain. Thus, under a constant stress (load), the straining process takes time to complete, and after the load is lifted, the recovery process also takes time and allows a certain degree of plastic (non-recoverable) deformation to take place. In addition, the amount of deformation is related to the duration of loading. Therefore an

impression may sustain deformation after being subjected to various forces during removal and then, in time, recovers most of the deformation after it is allowed to rest. This explains why removal of the impression should be done quickly (in a “snap”) if possible, and prolonged teasing or rocking should be avoided.

Polyvinyl siloxane impression materials exhibit the most elastic recovery of the currently available materials. Distortion on removal from undercuts is virtually nonexistent. However, the excellent elastic properties present a problem in that the heavy-body putty material begins to acquire elastic properties while it is still in the working-time stage. If the material is at an advanced stage of elasticity and is compressed excessively during the seating of the impression, distortion can occur when the material elastically rebounds (Figure 13-9).

The difficulty of removing earlier generations of polyether impressions from undercut areas is attributed to their high modulus of elasticity. The new generations of polyether impression materials, with a stiffness lower than that of hydrophilic PVS, were formulated specifically to address stiffness concerns. However, the inherent hydrophilicity of these polyethers has resulted in greater adhesion between the tissue and the material, which still makes impression removal difficult. It is important to note that increased precision also implies greater adaptation and resultant adhesion between the impression and the tissue, especially the teeth, and increased difficulty of removing the impression. Because of the reduced rigidity, these new generations of polyether impression material may not be the material of choice for the “triple-tray” technique, where the impression material's stiffness during removal compensates for the flexibility of the tray. Although these new polyether impression materials are flexible during removal, they have been shown to increase their elastic moduli for some time after removal. As the formulation of impression materials continues to evolve to accommodate specific needs, grouping the stiffness of impression materials based on the backbone of polymer chains is becoming less meaningful.



• **Figure 13-10** **A**, A properly retracted soft tissue will leave a narrow space to be filled by the light-viscosity impression material. **B**, The impression material has torn during removal.

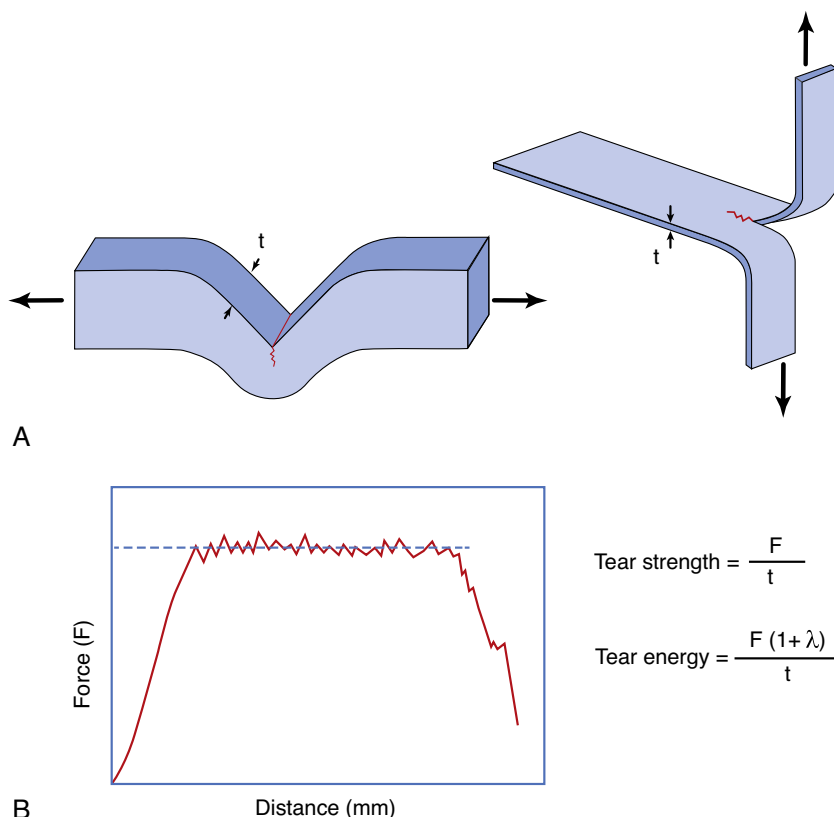
CRITICAL QUESTIONS

What is the difference between tear strength and tear energy? Why is tear energy more meaningful for impression making?

Tear Strength

The subgingival regions of the impression are often very thin and can tear during impression removal, leaving a portion embedded within the gingival sulcus (Figure 13-10). The tear strength is influenced by consistency and the manner of removing the materials. A heavier consistency usually increases the tear strength of the material. The addition of a thinning agent to the mixture reduces the tear strength slightly but increases the flexibility substantially. A quick snap in removing the impression usually increases the tear strength because the action increases the resistance of the material to deformation (strain).

Tear strength measures the resistance of an elastomeric material to fracture when subjected to a tensile force acting perpendicular to a surface flaw. Figure 13-11 shows two specimen designs that have been used by the dental community for testing impression materials. The amount of force needed to tear a specified test specimen, divided by the thickness of the specimen, is called the *tear strength*. Note that the calculation of tear strength disregards the dimensional change for the test specimen. For the same tooth preparation, a material that can be stretched a great deal elastically before fracture will likely remain intact, whereas a rigid material can fracture at a much lower tensile *strain* at a higher level of force. The latter will appear to have higher tear strength but is more likely to fracture than the former. Thus the use of tear strength to distinguish the resistance of an impression material to tearing is not very meaningful. The property that can delineate the combined behavior of stress and strain is energy (Chapter 4, *Resilience and Toughness*), which includes the dimensional change of the



• **Figure 13-11** **A**, Two configurations of tear-strength test specimens: right-angle design (left) and trouser design configuration (right). **B**, Force–distance curve of a typical tear test and calculation of tear strength and tear energy. The plateau of the curve (dotted line) indicates the force (F) needed for initiation and propagation of the crack. The thickness of the specimen is t, and the extension ratio is λ, which equals the extended portion of the specimen length at the end of the test divided by the original length of the specimen.

material in the calculation. The tear energy is determined by the force (F) needed to keep the crack propagating, the thickness of the specimen (t) and the extension ratio (λ). The extension ratio is the extended portion of the length (Δl) at the end of the test divided by the original length of the specimen (l) (Figure 13-11). The calculated value also has the units of N/m , which can be converted to $N \cdot m/m^2$ and then J/m^2 , an expression of energy per unit area.

Polysulfide materials have the highest resistance to tearing. Therefore thin sections of polysulfide impression material are less likely to tear than polyether or silicone impression materials of a similar thickness. However, because of their susceptibility to permanent distortion, polysulfide impressions may distort rather than tear. This presents a problem because tearing can be seen immediately by carefully checking the impression, whereas distortion is difficult to detect by visual inspection. Because the strain rate influences tear resistance and permanent deformation, the impression should be strained rapidly for as short a time as possible to minimize adverse effects.

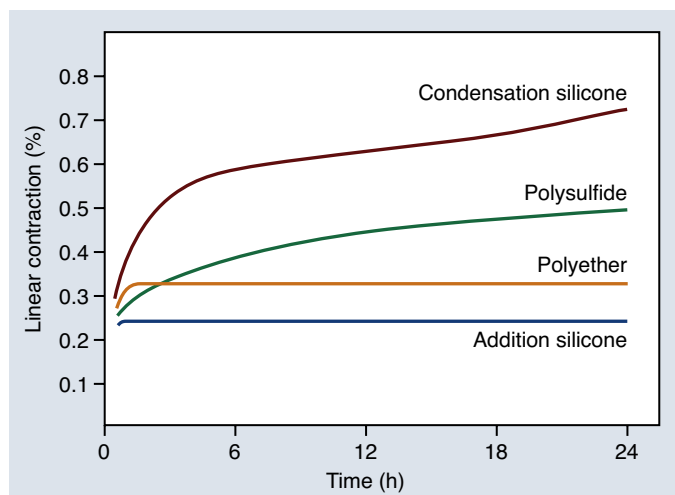
CRITICAL QUESTION

What are the main causes of impression inaccuracy?

Dimensional Stability

Dimensional stability refers to the lack of dimensional changes of the impression over time. There are six major sources of dimensional change: (1) polymerization shrinkage, (2) loss of a condensation reaction by-products (water or alcohol), (3) thermal contraction from oral temperature to room temperature, (4) absorption of water or disinfectant over a period of time, (5) incomplete recovery of deformation because of viscoelastic behavior, and (6) incomplete recovery because of plastic deformation. Figure 13-12 shows the mean linear contraction for four elastomers using the method described in American National Standards Institute American Dental Association (ANSI/ADA) Specification No. 19 and ISO 4823.

Figure 13-12 shows that if maximal accuracy is to be maintained, the slurry mix for a stone die or cast should be poured within the first 30 minutes after the polysulfide and condensation silicone impression are removed from the mouth. The stability of the addition silicone and polyether materials suggests that these impressions



• **Figure 13-12** Representative linear contraction of four elastomeric impression materials.

do not have to be poured with a gypsum product immediately. Research has shown that pouring between 24 hours and 1 week produced casts as accurate as those made in the first hour. Multiple pouring of the impressions and removal of the casts will not alter the dimensional stability of the impression, even though a substantial force is needed each time a cast is removed from the impression.

One variable that can have a negative effect on the polyether impression is the absorption of water or fluids and the simultaneous leaching of the water-soluble plasticizer during disinfectant immersion longer than 10 minutes. However, recent research has shown that 30-minute immersion does not have a negative effect on the dimensions. Nonetheless, the polyether impression should be stored in a dry (relative humidity below 50%), cool environment to maintain its accuracy and should never be left for protracted periods in disinfecting solutions.

CRITICAL QUESTION

Why are hydrophilic materials potentially more susceptible to distortion during disinfection prior to being poured with a gypsum-forming product?

Disinfection

All elastomeric impression materials can be disinfected with all disinfectants registered with the U.S. Environmental Protection Agency (EPA) without the loss of surface quality or accuracy if the disinfection time is short. The impressions should be immersed for the time specified for each disinfectant, as discussed in the last section. After disinfection, the impression should be removed, rinsed, and poured with the gypsum product as soon as possible.

Table 13-4 shows a guide for selecting appropriate disinfection methods for all types of impressions that are subsequently transferred to a dental laboratory.

CRITICAL QUESTION

How does the surfactant added to hydrophilize PVS affect the contact angle of water droplets during the setting and pouring of casts with gypsum?

Wettability of Impression Materials and Hydrophilization of PVS

The contact angles of distilled water on set silicone impressions are approximately 100° , which makes this group of materials the most hydrophobic among all elastomeric impression materials. The use of a more hydrophobic impression material may lead to a high frequency of voids in the cast. It is possible to spray a surfactant on these hydrophobic impressions prior to pouring with gypsum mixtures. A nonionic surfactant may be added to the bulk of the PVS during the manufacturing process, and the resultant material is called a *hydrophilized* PVS.

In vitro studies of the surface wettability of set impressions typically use distilled water as the probing liquid. The results confirm that there are significant reductions in the contact angles of hydrophilized PVS relative to their nonhydrophilized counterparts. The use of an aqueous solution saturated with $CaSO_4$ yields similar results. Examination of stone casts confirms that elastomers, which exhibit the least contact angle with water, also produce stone casts with fewer voids.

The use of optical tensiometry, which analyzes the shape of liquid drops on the surface using a video image, allows observation of the contact angles of water droplets on freshly mixed impression materials in real time. Numerous studies have reported a decrease in water contact angles on silicones, hydrophilized PVS,

TABLE 13-4 Guide for the Selection of Appropriate Disinfection Methods for Impressions Transported to a Dental Laboratory

Material	Method	Recommended Disinfectant	Comments
Alginate	Immersion with caution Use only disinfectant for a short-term exposure time (<10 min for alginate)	Chlorine compounds or iodophors	Short-term glutaraldehyde has been shown to be acceptable, but time is inadequate for disinfection.
Agar			Do not immerse in alkaline glutaraldehyde!
Polysulfide and silicone	Immersion	Glutaraldehydes, chlorine compounds, iodophors, phenolics	Disinfectants requiring more than 30-min exposure times are not recommended.
Polyether	Immerse with caution Use disinfectant only for a short exposure time (<10 min)	Chlorine compounds or iodophors	ADA recommends any of the disinfectant classes; however, short-term exposures are essential to avoid distortion.
ZOE impression paste	Immersion preferred; spraying can be used for bite registrations	Glutaraldehydes or iodophors	Not compatible with chlorine compounds! Phenolic spray can be used.

ADA, American Dental Association; ZOE, zinc oxide–eugenol.

and polyethers over the setting period. This decrease can be as much as 70° for hydrophilized PVS and less for polyether. Chemical analyses of water droplets show that they all acquire substances from their respective impression materials. For hydrophilized PVS, the water droplets absorb a sufficient quantity of surfactant and become a liquid of lower surface tension. The lowering of surface tension makes water droplets spread wider on the surface of PVS, yielding lower contact angles. This observation leads to the hypothesis that hydrophilicity of the PVS does not change much, but the acquired surfactant has reduced the surface tension of the probing water, making it readily spread over the PVS. Some clinical observations seem to support this hypothesis because there is no difference between nonhydrophilized and hydrophilized PVS with respect to the reproducibility of detail on wet surfaces. However, another clinical study reports that hydrophilized PVS yields a significantly higher proportion of void-free impressions than its nonhydrophilized counterpart. For polyethers, the substances acquired by the water droplets represent a low-molecular-weight compound associated with polyethers, and their effect on the surface tension of the water droplet is small. Thus a smaller decrease in the contact angle is observed.

As soon as hydrophilized PVS encounters oral fluids during impression making, it begins to release surfactant to its surroundings. It is known that there is an adequate amount of surfactant trapped on the surface of set PVS impressions, thereby providing hydrophilicity for the pouring of gypsum dies. Whereas one might believe that the decrease of contact angle over the period of setting is equivalent to good wetting of the impression material on moist tooth surfaces, the clinical relevance remains unclear for two reasons. First, the decrease in contact angle may be attributed mainly to the lowering of the surface tension of the water droplets by the surfactant, so the actual improvement in the hydrophilicity of the impression may be much less significant than it appears. Second, there are conflicting clinical observations. This conflict is not surprising when one realizes that some materials contain very hydrophilic surfactants that are readily leached from the surface, whereas others contain surfactants that are balanced in their hydrophilic and lipophilic properties so that the lipophilic end remains buried near the surface while the hydrophilic chain is exposed on the surface. In the latter case, very little leaching occurs.

Effect of Mishandling

The failure to produce an accurate epoxy or gypsum die or cast is more likely associated with an error in handling rather than a deficiency in the properties of the impression material. The common failures experienced with impression materials and their causes are summarized in Table 13-5. A summary of the characteristics of the elastomeric impression materials is given in Table 13-6.

CRITICAL QUESTION

What is the difference between a solution and a hydrocolloid?

Hydrocolloids

A **colloid** is a substance that is microscopically dispersed uniformly throughout another medium. This is different from a solution, as defined in Chapter 2, **Solutes and Solvents**. A solution is a single phase, whereas a colloidal system consists of the dispersed phase and the dispersion phase. If the dispersion phase of a colloidal system is water, it is called a *hydrocolloid*. The sizes of the colloid particles range from 1 to 200 nm.

Success in impression making depends on the transformation from a flowable state to a solid elastomeric state. This change of state with hydrocolloids is called the *sol–gel transformation*. A *sol* is a colloidal dispersion in a continuous liquid medium, and a **gel** is a suspension that behaves like an elastic solid. If a hydrocolloid contains an adequate concentration of the dispersed phase, the sol, under certain conditions, may change to a gel. In the gel state, the dispersed phase forms agglomerates in the form of chains or fibrils, also called micelles. The fibrils may branch and intermesh to form a brush-heap structure, which can be envisioned as resembling the intermeshing of tree branches or twigs in a brush pile. The dispersion medium is held in the interstices between the fibrils by capillary attraction or adhesion. In this section, the characteristics of the two hydrocolloids used for impression making, agar and alginate, are described.

Agar (Reversible Hydrocolloid)

The sol–gel transformation of agar is a physical phenomenon induced by temperature change. The gel liquefies when it is heated to 70 to 100 °C, which is known as the *liquefaction temperature*,

TABLE 13-5 Common Failures Occurring With the Use of Elastomeric Impression Materials

Type of Failure	Causes
Rough or uneven impression surface	Incomplete polymerization caused by premature removal from the mouth, improper ratio or mixing of components, or presence of oil or other organic material, such as plaque, on the teeth For addition silicone, surface agents, such as latex, that contaminate the material and inhibit polymerization Too rapid polymerization from high humidity or temperature Excessively high accelerator/base ratio with condensation silicone
Bubbles	Air incorporated during hand mixing
Irregularly shaped voids	Moisture or debris on surface of teeth
Rough or chalky stone cast	Inadequate cleaning of impression Excess water that is not blown off the impression Excess wetting agent left on impression Premature removal of cast; improper powder/water ratio of stone Failure to delay pour of addition silicone that does not contain a palladium salt for at least 20 min
Distortion	Resin tray not aged sufficiently; still undergoing polymerization shrinkage Lack of adhesion of elastomer to the tray caused by not applying enough coats of adhesive, filling tray with material too soon after applying adhesive, or using incorrect adhesive Lack of mechanical retention to the impression tray Excessive bulk of material Insufficient relief for the reline material (if such technique is used) Development of elastic properties in the material before tray is fully seated Continued pressure against impression material that has developed elastic properties Movement of tray during polymerization Premature removal of impression from mouth Improper removal of impression from mouth Delayed pouring of the polysulfide or condensation silicone impression

TABLE 13-6 Characteristics of Elastomeric Impression Materials

Generic Type	Advantages	Disadvantages
Polysulfide	Long working time High tear resistance Margins easily seen Moderate cost	Requires custom tray Stretching leads to distortion Compatible with stone Stains clothing Obnoxious odor Pour within 1 h
Condensation silicone (putty wash)	Putty for custom tray Clean and pleasant Good working time Margins easily seen	High polymerization shrinkage Volatile by-product Low tear strength Hydrophobic Pour immediately
Vinyl polysiloxane	One material Putty for custom tray Automix dispense Clean and pleasant Margins easily seen Ideally elastic Pour repeatedly Stable; delay pour	Hydrophobic No flow if sulcus is moist Low tear strength Putty displaces wash Wash has low tear strength Putty too stiff Putty and wash separate Difficult to pour cast
Polyether	Fast-setting Clean Automix dispense Least hydrophobic of all elastomers Margins easily seen Good stability Delay pour Shelf life: 2 y	Stiff, high modulus Bitter taste Need to block undercuts Absorbs water Leaches components High cost

TABLE 13-6 Characteristics of Elastomeric Impression Materials—cont'd		
Generic Type	Advantages	Disadvantages
Agar	Moist field OK Accurate and pleasant Hydrophilic Low cost Long shelf-life	Requires special equipment Thermal discomfort Tears easily Pour immediately Difficult to see margins and details
Alginate	Moist field OK Clean and pleasant Hydrophilic Low cost Long shelf-life	Not accurate/rough Tears easily Pour immediately Can retard setting of gypsum

and the sol solidifies around 37 to 50 °C, which is known as the **gelation** temperature. Thus agar is called a *reversible hydrocolloid*. The gelation temperature is critical for impression making. If it is too high, the heat from the sol may injure the oral tissues. Conversely, if the gelation temperature is too far below oral temperature, it will be impossible to make the impression because the sol will not convert to a gel in the oral cavity.

Composition

Agar, a polysaccharide, is the main active ingredient in the material, whereas water is the major constituent in the agar impression material. Various fillers—such as borax, diatomaceous earth, clay, silica, wax, rubber, and similar inert powders—are used to control strength, viscosity, and rigidity, as previously discussed for elastomeric impression materials. Thymol and glycerin may also be added as a bactericidal agent and plasticizer, respectively. Pigments and flavors are usually included as well. The hydrocolloid is usually supplied in two forms, syringe material and tray material.

CRITICAL QUESTION

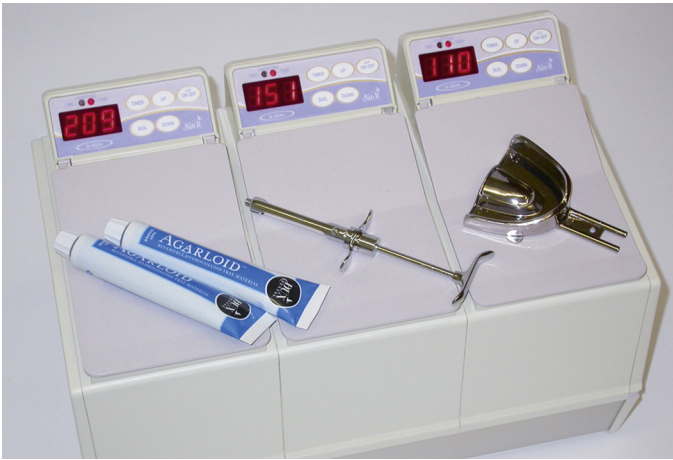
What is the purpose of having three water tanks set at three different temperatures in a conditioning unit for agar impression materials?

Making Agar Impression

This process requires a three-compartment conditioning unit (Figure 13-13) for the agar tray material that allows liquefaction, storage, and tempering; the agar syringe material is used only in the liquefaction and storage compartments.

The first step in impression making is to liquefy the hydrocolloid gel in the tube in boiling water at 100 °C. The tube is then placed in a storage bath at 65 °C to retain the sol condition until it is needed. For the immediate preparation step, the impression tray is filled with hydrocolloid sol from the tube taken from the storage bath, a gauze pad is placed over the top of the tray material, and the tray is placed in the tempering compartment (at about 45 °C). The tempering time is 3 to 10 minutes, just sufficient to ensure that all the material has reached a low temperature of 55 °C or less. In any case, the loaded tray should never be left in this bath for more than 10 minutes because partial gelation can occur, thereby making the material unusable.

Just before tempering of the tray material is completed, the syringe material is taken directly from the storage compartment and applied to the prepared teeth. The syringe material is never tempered because it must be maintained in a fluid state to enhance adaptation to the

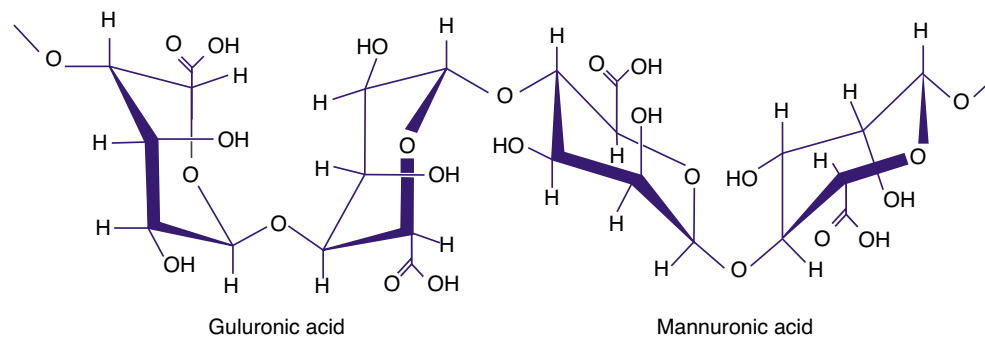


• **Figure 13-13** Conditioning unit for agar impression materials. The three compartments are used for liquefying the material (*left*), storing after boiling (*middle*), and tempering the tray hydrocolloid (*right*). The number on the display shows the temperature setting in °F. Also shown in the figure are the tray hydrocolloid, a syringe for injecting hydrocolloids, and an impression tray. Note that the two tubes extending out from the handle of the tray are for water circulation.

tissues. Normally, the temperature of the syringe material is cooled sufficiently as it is extruded, so it is comfortable for the patient. The syringe material is first applied to the base of the preparation; then the remainder of the prepared tooth is covered. The tip of the syringe is held close to the tooth, and it remains embedded below the surface of the syringe material to prevent entrapment of air bubbles. The water-soaked outer layer of the hydrocolloid-loaded tray and the gauze covering the tray impression material are removed to ensure firm bonding to the syringe hydrocolloid. The tray is immediately brought into position, seated with light pressure, and held with a very light force. Too much pressure may displace the syringed agar sol from the tooth and distort the impression.

Gelation is accelerated by circulating cool water (approximately 18 to 21 °C) through the tray for 3 to 5 minutes. During the gelation process, the tray must be held in the mouth until gelation has proceeded to a point at which the gel strength is sufficient to resist deformation or fracture.

As discussed earlier in the section on elastomeric impression materials, hydrocolloid materials exhibit viscoelastic behavior; therefore it is necessary to remove the impression with a snap and not to tease it out. Any twisting or flexure should be avoided. When properly done, the resulting impression will



• **Figure 13-14** Structural formula of alginic acid. Alginic acid is a linear copolymer with homopolymeric blocks of β -D-mannuronic acid and its epimer α -L-guluronic acid covalently linked together in different sequences or blocks.

TABLE 13-7 Powder Composition for an Alginate Impression Material

Component	Function	Weight Percentage
Potassium alginate	Soluble alginate	15
Calcium sulfate	Reactor	16
Zinc oxide	Filler particles	4
Potassium titanium fluoride	Gypsum hardener	3
Diatomaceous earth	Filler particles	60
Sodium phosphate	Retarder	2

accurately reproduce the dimensions and details of hard and soft tissues.

Distortion During Gelation

Some contraction occurs because of the physical change during the sol–gel transformation. If the material is held firmly in the tray, the impression material will shrink toward the center of its mass, thereby creating larger dies. Because the sol is a poor thermal conductor, rapid cooling may cause a stress concentration near the tray where the gelation first takes place. Consequently, water at room temperature is more suitable for cooling the impression than is ice water.

Alginate (Irreversible Hydrocolloid)

The setting of alginate hydrocolloid is a process of crosslinking alginic acids with calcium ions. The alginic acid, which is extracted from brown seaweed, is a linear copolymer of β -D-mannuronic acid and α -L-guluronic acid (Figure 13-14). Alginates with higher levels of guluronic acid normally show a stronger interaction with calcium and, hence, yield greater gel strength. For impression-making purposes, the alginate is richer in mannuronic acid.

Composition

The chief active ingredient in the alginate impression materials is one of the soluble alginates, such as sodium, potassium, or triethanolamine alginate. Table 13-7 shows a formula for the powder component of an alginate impression material. The diatomaceous earth acts as a filler to increase the strength and stiffness of the

alginate gel. It also produces a smooth texture and ensures the formation of a firm gel surface that is not tacky. Zinc oxide also acts as a filler and has some influence on the physical properties and setting time of the gel. Calcium sulfate dihydrate is a reactor providing calcium ions that crosslink the alginate sol. A retarder is added to control the setting time. A fluoride, such as potassium titanium fluoride, is added as an accelerator for the setting of the stone to ensure a hard, dense cast surface when the stone sets in the impression. This fluoride is also called a *surface hardener*.

When powder in the alginate can is fluffed to break the particles loose, the diatomaceous earth, which is made up of fine porous silica particles, will become airborne when the lid is removed. Long-term exposure through inhalation of these fine silica particles can cause silicosis and pulmonary hypersensitivity. To reduce the dust encountered after tumbling, manufacturers have introduced a “dustless” alginate in which they have incorporated polyethylene glycol or polypropylene glycol in the alginate powder to agglomerate the particles. This causes the powder to become denser and less able to become airborne. Color indicators have been added in some formulations to reveal the stage of the setting reaction. This is to assist the operator in deciding when to proceed to the next step of impression making.

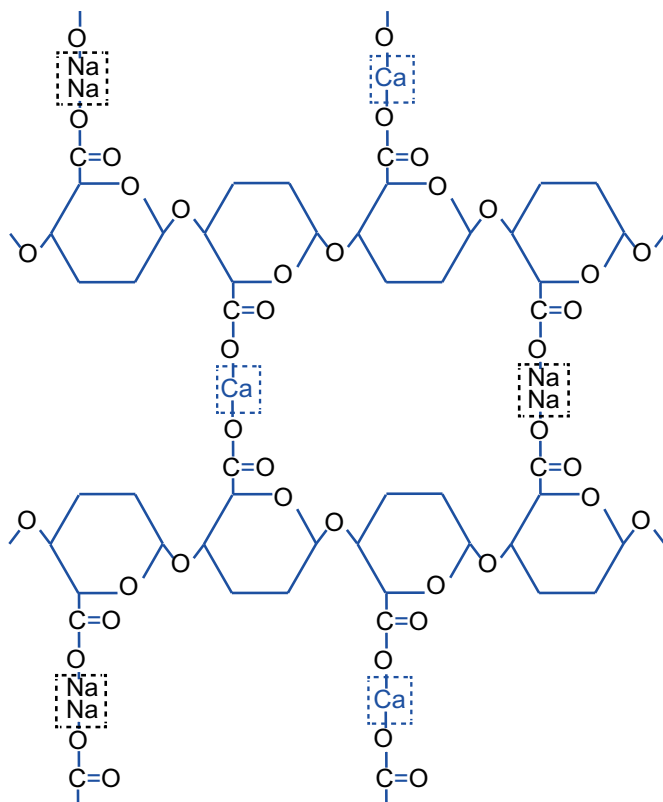
Two-paste alginate impression materials are also available; these are known as *modified alginates*. One paste contains a sol of alginate, fillers, retarder, and other ingredients like glycols and dextrose. The other paste consists of gypsum dihydrate, fillers, retarder, glycerol or glycols, gypsum surface modifier, and some silicone oil.

CRITICAL QUESTION

How does the retarder optimize the working time of alginate impression material?

Gelation Process

The typical sol–gel reaction can be described simply as a reaction of soluble alginate with calcium ions from calcium sulfate and the formation of an insoluble calcium alginate. Structurally, calcium ions replace the sodium or potassium ions of two adjacent molecules to produce a crosslinked complex or polymer network (Figure 13-15). The production of the calcium alginate is so rapid that it does not allow enough working time. A water-soluble phosphate salt (e.g., trisodium phosphate) is added to the composition as a retarder to extend the working time. The strategy is that the calcium ions react preferentially with the phosphate ions in the solution. Thus the rapid reaction between calcium ions and



• **Figure 13-15** Schematic illustration of sodium alginate crosslinked with calcium ions. The base molecules represent the sodium salt of alginic acid, in which hydrogen atoms of carboxyl groups are replaced by sodium atoms. Apart from polar groups, all side chains have been omitted for simplification.

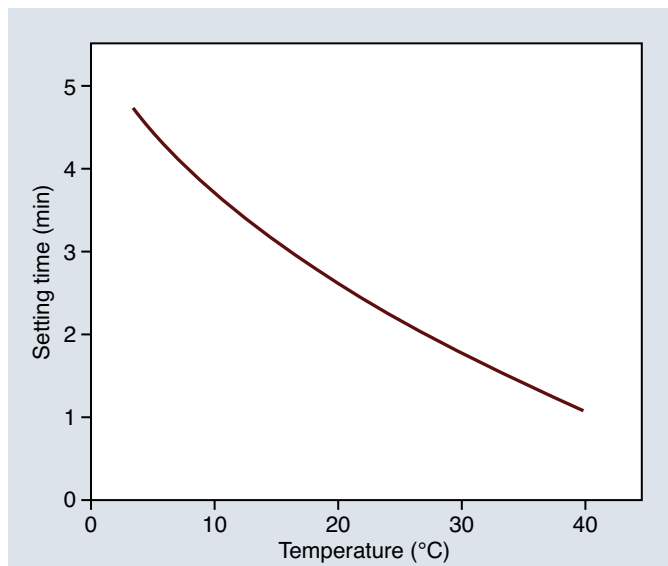
the soluble alginate is deferred until phosphate ions from trisodium phosphate are exhausted. The amount of retarder is adjusted to provide the stated setting time.

Controlling Setting Time

A slight modification in the water–powder (W/P) ratio or the mixing time can have marked effects on two important properties of the gel, tear strength and elasticity; thus the setting time is best regulated by the amount of retarder added during the manufacturing process. Usually, the manufacturers make both fast-setting alginate (1.5 to 3 minutes) and normal-setting alginate (3 to 4.5 minutes) to give clinicians a choice of the materials that best suit their working style.

Clinicians, however, can safely influence the setting time by altering the temperature of the water (Figure 13-16). The temperature of the mixing water should be controlled carefully within a degree or two of a standard temperature, usually 20 °C, so that a constant and reliable setting time can be obtained. In hot weather, special precautions should be taken to provide cool water for mixing so that premature gelation does not occur. It may even be necessary to precool the mixing bowl and spatula, especially when small amounts of impression material are to be mixed.

Tap water naturally contains certain quantities of metallic ions, primarily calcium and magnesium. It has been shown that compared with distilled water for mixing of alginate impression material, the use of tap water with a high hardness may accelerate the setting of the alginate. If one observes that the setting time has decreased in



• **Figure 13-16** Effect of water temperature on the setting time of an alginate impression material.

a new office or clinic location, the effect of the hardness of the tap water on setting time should be considered as a possible cause.

CRITICAL QUESTION

Why is it especially important to add water to the rubber mixing bowl before adding the powder when one is mixing a fast-setting alginate impression material?

Preparation of Alginate Impression Materials

The measured powder is added slowly to the premeasured water that has already been poured into a clean rubber bowl. The powder is incorporated into the water by carefully mixing with a metal or plastic spatula that is flexible to adapt well to the wall of the mixing bowl. If the powder is placed in the mixing bowl first, penetration of the water to the bottom of the bowl is inhibited, and a longer mixing time may be required to ensure a homogeneous mix. Care should be taken to avoid incorporating excessive air into the mix. A vigorous figure-eight stropping motion is best, with the mix being wiped or stropped against the side of the rubber-mixing bowl to express air bubbles. All the powder must be incorporated thoroughly in the water.

The mixing time is particularly important; 45 seconds to 1 minute is generally enough, depending on the brand and type of alginate (fast set or regular set). The instructions on the package should be followed precisely for the mixing time, working time, and setting time for the material one is using. The result should be a smooth, creamy mixture that does not readily drip off the spatula when it is raised from the bowl. Several mechanical mixing devices are available for the alginate materials. They include a rotating mixing bowl; a mechanical mixer with a time-control unit; a vacuum mixer for powder/water mixing; and a dynamic mechanical mixer, like the one for elastomers (Figure 13-7, D), for two-paste alginate products. Their principal benefits are convenience, speed, and the reduction of human error.

Clean equipment is important; contaminants, such as small amounts of gypsum left in the bowl from a previous mix of plaster or stone, can accelerate the set. It is best to use separate bowls for mixing alginate and stone.

Ideally, the powder should be weighed and not measured by volume using a scoop. However, unless a grossly incorrect or inconsistent method is used for scooping the powder, the variations in individual mixes should have no measurable effect on the physical properties.

Making Alginate Impression

It is imperative that the impression be retained on the tray so that it can be withdrawn from the perimeter of the teeth. Therefore a perforated metal tray is preferred. If a plastic tray or a metal rim-lock tray is selected, a thin layer of alginate tray adhesive should be applied and allowed to dry completely before mixing and loading the alginate in the tray. Alginate is a weak material; therefore a sufficient bulk of material is needed. The thickness of the alginate impression between the tray and the tissues should be at least 3 mm.

Most set alginate materials improve in elasticity over time; this minimizes distortion of the material during impression removal, thus permitting superior reproduction of undercut areas. Data clearly indicate that the alginate impression should not be removed from the mouth for at least 3 minutes after gelation has occurred. It is possible to leave an alginate impression in the mouth too long. With certain alginates, it has been shown that if the impression is held for 6 to 7 minutes after gelation rather than 3 minutes, significant distortion may result.

Because alginate is a viscoelastic material, the speed of removal must be a compromise between a rapid movement and a slower rate that is more comfortable for the patient. Usually an alginate impression does not adhere to the oral tissues as well as some of the elastomers do, so it is easier to break the seal ("suction") first and then remove the alginate impression rapidly. It is always best to avoid torqueing or twisting the impression to remove it quickly.

Strength

Any deviation from the manufacturer's instructions can have adverse effects on the gel strength. For example, if too much or too little water is used in mixing, the final gel will be weakened, making it less elastic. Insufficient spatulation results in failure of the ingredients to dissolve sufficiently so that the chemical reactions can proceed uniformly throughout the mass. Overmixing breaks up the formation of the calcium alginate network and reduces its strength.

Shelf Life

Two major factors that affect the shelf life of alginate impression materials are storage temperature and moisture contamination from ambient air. The alginate impression powder can be purchased in individually sealed bags or in bulk form in a can. The individual bags are preferred because there is less chance for contamination during storage and the correct W/P ratio is ensured. Nevertheless, the bulk form in a can is by far the most popular. If the bulk powder form of alginate is used, the lid should be firmly replaced on the container as soon as possible after dispensing the powder so that moisture contamination is minimized.

An expiration date under a stated condition of storage should be clearly identified by the manufacturer on each package. It is best not to stock more than a year's supply in the dental office. The material should be stored in a cool, dry environment.

Properties of Hydrocolloid Impression Materials

The quality of a stone cast depends on the properties of the hydrocolloid impressions before pouring and the potential interaction between gypsum and alginate during the setting of the gypsum. In this section, details on dimensional stability, gypsum/hydrocolloid interaction, accuracy, disinfection, and effects of mishandling are described.

CRITICAL QUESTION

How can distortion of a hydrocolloid impression be minimized during storage?

Dimensional Stability

Once the hydrocolloid impression is removed from the mouth and exposed to air at room temperature, some shrinkage associated with **syneresis** and evaporation will occur. Conversely, if the impression is immersed in water, swelling caused by **imbibition** can occur. Figure 13-17 shows that the material has shrunk in air and excessive expansion has occurred during subsequent imbibition.

Thermal changes also contribute to dimensional change. With alginates, impressions shrink slightly because of the thermal differential between mouth temperature (37 °C) and room temperature (23 °C). The agar hydrocolloids experience a temperature shift in the opposite direction, from the chilled, water-cooled tray (15 °C) to the warmer room temperature. Even this slight change can cause the impression to expand and become less accurate.

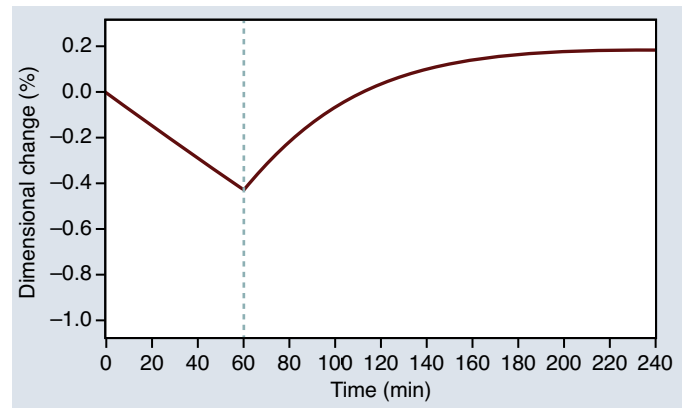
If pouring of the impression must be delayed, the impression should be rinsed in tap water, disinfected, wrapped in a surgical paper towel, saturated with water, and placed in a sealed plastic bag or humidior.

CRITICAL QUESTION

Why do both agar and alginate include a gypsum hardener, and how does it function?

Compatibility With Gypsum

Agar impression material contains borax, which is a known retarder for the setting of gypsum products. The gelation process of alginate impressions produces not only insoluble calcium alginate but also sodium sulfate, which is a gypsum-setting accelerator at low concentration but becomes a retarder at a higher concentration. In addition, polysaccharide also inhibits the setting of gypsum. Because of retardation, the surfaces of the gypsum models prepared from hydrocolloid may be too soft for use as dies or casts.



• **Figure 13-17** Linear contraction of a representative reversible hydrocolloid in air (31% to 42% relative humidity) within the initial and subsequent expansions in water. The dashed line indicates the start of water immersion.

The deficiency of gypsum setting can be overcome by immersing agar impressions in a solution containing a gypsum setting accelerator, such as 2% potassium sulfate solution, prior to pouring the impression with the gypsum-forming product or by incorporating a gypsum surface hardener, such as potassium titanium fluoride, in alginate (Table 13-7). The solubility of potassium titanium fluoride is about 1.3 g per 100 mL of water at 20 °C. The fluoride on the surface of alginate will form fine calcium fluoride precipitates with the calcium from the gypsum. Fine calcium fluoride particles become nuclei that accelerate the setting of gypsum.

A rough stone surface will result if excess rinsing water has collected on the surface of the impression at the time of pouring the stone mixture. A dried gel surface, on the other hand, will result in its adherence to the surface of the cast, which can result in tearing upon its removal. The surface of the impression should be shiny but with no visible water film or droplets at the time of pouring. After the impression has been filled with stone, somewhat superior stone surfaces may be obtained if the impression is placed in a humidor while the stone hardens.

The stone cast or die should be kept in contact with the impression for a minimum of 30 minutes, preferably for 60 minutes, before the impression is separated from the cast. A longer time may be needed for slow-setting gypsum. It is wise to separate the cast from the impression within a reasonable time so that desiccation of the hydrocolloid does not occur, thereby avoiding abrasion of the gypsum cast during its removal.

CRITICAL QUESTION

What is the optimal method for disinfecting an alginate hydrocolloid impression without causing significant distortion or degradation?

Disinfection

Because the hydrocolloid impression must be poured within a short time after removal from the mouth, the disinfection procedure should be relatively rapid to prevent a dimensional change. The current protocol for disinfecting hydrocolloid impressions recommended by the Centers for Disease Control and Prevention is to use household bleach (1-to-10 dilution), iodophors, or synthetic phenols as disinfectants. After the impression has been rinsed thoroughly, the disinfectant can be sprayed liberally on the exposed surface. The impression is then immediately wrapped in a disinfectant-soaked paper towel and placed in a sealed plastic bag for 10 minutes. Finally, the wrapped impression is removed from the bag, unwrapped, rinsed, and shaken to remove excess water. The impression is then poured with the stone of choice. An alternative disinfection method is by immersion, but this should not exceed 10 minutes (Table 13-4).

Accuracy

Agar is among the most accurate of impression materials. Most alginate impressions are not capable of reproducing the finer details observed in impressions with other elastomeric impression materials. Nevertheless, alginate materials are sufficiently accurate that they can be used to make impressions for removable partial dentures.

Effects of Mishandling

Common causes of failures encountered with alginate impression materials are summarized in Table 13-8.

Duplicating Materials

Both types of hydrocolloids are used in the dental laboratory to duplicate dental casts or models for the construction of prosthetic appliances and orthodontic models. Agar hydrocolloid is more popular in

TABLE 13-8 Common Causes of Failed Hydrocolloid Impressions

Effect	CAUSES	
	Agar	Alginate
Grainy material	Inadequate boiling Storage temperature too low Storage time too long	Improper mixing Prolonged mixing Excessive gelation Water/powder ratio too low
Separation of syringe materials	Water-soaked tray material surface not removed material Premature gelation of either material	Not applicable
Tearing	Inadequate bulk Premature removal from mouth Syringe material partially gelled when tray was seated	Inadequate bulk Moisture contamination Premature removal from mouth Prolonged mixing
External bubbles	Gelation of syringe material, preventing flow	Undue gelation preventing flow Air incorporated during mixing
Irregularly shaped voids	Material too cold	Moisture or debris on tissue
Rough or chalky stone model	Inadequate cleansing of impression Excess water or hardening solution left in the impression Premature removal of die Improper manipulation of stone Air drying of the impression before pouring	Inadequate cleaning of impression Excess water left in impression Premature removal of the impression Model left in impression too long Improper manipulation of stone
Distortion	Impression not poured within 30 min Movement of tray during gelation Premature removal from mouth Improper removal from mouth Use of ice water during initial stages of gelation	Impression not poured immediately Movement of tray during gelation Premature removal from mouth Improper removal from mouth

the lab because it can be used many times. In addition, with intermittent stirring, agar hydrocolloid can be kept in a liquid form for 1 or 2 weeks at a constant pouring temperature. These factors make the cost of reversible impression materials quite reasonable.

The hydrocolloid-type duplicating materials have the same composition as the impression materials, but their water content is higher. Consequently, the agar or alginate content is lower, which influences their compressive strength and percent permanent set. These property requirements are identified in ISO 14356:2003, Dentistry—Duplicating material.

Inelastic Impression Materials

Inelastic impression materials are brittle materials that exhibit an insignificant amount of elastic deformation before fracture. They include impression plaster, impression compound, and ZOE impression paste. Because of their limited use in clinical dentistry today, the discussion is brief and focused on compositions and applications.

Impression Plaster

Impression plaster is a β -calcium sulfate hemihydrate powder (to be discussed in the following section) mixed with water at a ratio of 100 g powder to 50 to 60 mL of water. Its fluidity makes it suitable for making impressions of soft tissues in the uncompressed state, a characteristic of mucostatic impression material. Freshly mixed plaster is too fluid to be retained in a stock tray; a custom tray is needed. Preliminary impressions can be made with dental compound, and impression plaster can be used as the wash material, which is the same concept as in the putty-wash technique.

Historically, impression plaster had been used to make impressions of hard tissue before the era of elastic impression materials. The clinician broke the plaster impression to facilitate removal of the impression and reassembled the fragments to form a completed impression ready for pouring the cast. A separate medium was applied on the impression to keep the cast from merging with the impression plaster. The impression would be fractured again to retrieve the cast.

Impression Compound

Impression compound, also called *modeling plastic*, is a thermoplastic material composed of waxes, thermoplastic resins, filler, and a coloring agent. The low thermal conductivity of these materials indicates the need to allow an extended time to achieve uniform softness, thorough heating, and thorough hardening to withdraw the impression from the mouth.

Type I is a lower-fusing material for making impressions of a single tooth or for border molding of an acrylic custom tray

during the fitting of the tray. A compound stick may be softened over a flame, but the sheet should be immersed in warm water to ensure uniform softening of the material. The compound should not be allowed to boil or ignite over the flame, and prolonged immersion or overheating in the water can alter the chemistry of the compound and the properties. Cold water can be sprayed on the compound to assist in cooling.

Type II is a higher-fusing material in sheet form, also called *tray compound*, and can be used to make primary impressions of soft tissue to be used as a tray to support a thin layer of a second impression material, such as ZOE wash paste, hydrocolloid, impression plaster, or elastomer, to make the secondary impression of the soft tissue.

CRITICAL QUESTION

Why does ZOE set faster in a humid environment?

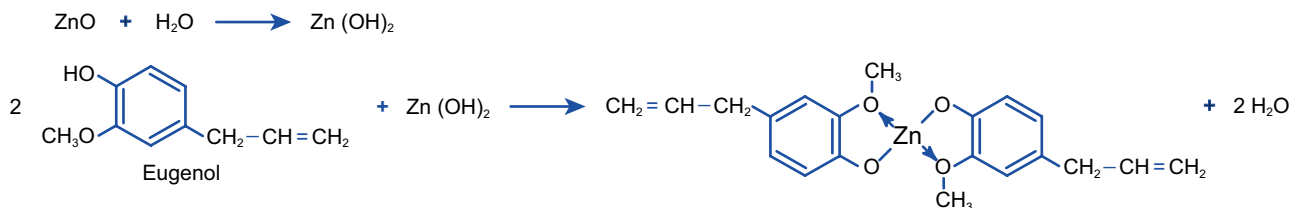
Zinc Oxide–Eugenol Impression Paste

The reaction between zinc oxide and eugenol yields a relatively hard mass that has been involved in a wide range of applications in dentistry, including use as an impression material for edentulous mouths, a surgical dressing, a bite registration paste, a temporary filling material, a root canal filling material, a cementing medium (Chapter 7, Zinc Oxide Eugenol and Non-Eugenol Cements), and a temporary relining material for dentures.

ZOE impression pastes are dispensed as two pastes. One tube contains zinc oxide and vegetable or mineral oil; the other contains eugenol, rosin, filler, and resinous balsam. The vegetable or mineral oil acts as a plasticizer and aids in offsetting the action of the eugenol as an irritant. The addition of rosin facilitates the speed of the reaction and yields a smoother, more homogeneous product. Resinous balsam is often used to increase flow and improve mixing properties.

The setting reaction requires an ionic medium in which it can proceed at any desired rate. It is well established that the first reaction is the hydrolysis of zinc oxide to its hydroxide (Figure 13-18). In formulations that do not contain water in the paste, the setting of the material is retarded until the mixed paste encounters moisture in the patient's mouth. In any case, water provides additional acceleration. One of the chief disadvantages of the ZOE pastes is the possible stinging or burning sensation caused by the eugenol as it leaches out and contacts soft tissues.

Mixing of the two pastes is accomplished on an oil-impervious paper or glass mixing slab. The proper proportion of the two pastes is generally obtained by squeezing two strips of paste of the same length, one from each tube, onto the mixing slab. A flexible stainless-steel spatula is typically used for the mixing procedure. The two strips of contrasting colors are combined with the first stroke of the spatula, and the mixing is continued for approximately 1 minute, or as directed by the manufacturer, until a uniform color is achieved.



• **Figure 13-18** Setting reaction of zinc oxide–eugenol. Arrows between zinc and oxygen of methoxy groups indicate coordinate bonds.

These materials are classified as a hard paste (type I) or soft paste (type II). The final set should occur within 10 minutes for a type I paste (hard) and 15 minutes for a type II paste (soft). When the final set occurs, the impression can be withdrawn from the mouth. The actual time will be shorter when setting occurs in the mouth because humidity and temperature can accelerate the setting reaction.

A paste of a thick consistency (high viscosity) can compress the tissues, whereas a thin, fluid material results in an impression that captures a negative replica of the tissues in a relaxed condition with little or no compression. In any event, the impression paste should be homogeneous. Pastes of varying consistencies are commercially available. An advantage of a heavier-consistency material is its increased strength.

The dimensional stability of the impression pastes is quite satisfactory. A negligible shrinkage (less than 0.1%) may occur during hardening. No significant dimensional change subsequent to hardening should occur with high-quality commercial products. The impressions can be preserved indefinitely without the change in shape that can result from relaxation or other causes of warping. This condition can be satisfied only if the tray material is dimensionally stable.

Gypsum Products

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; calcium sulfate dihydrate) is a mineral mined in various parts of the world. Gypsum products are supplied as fine hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) powders that are produced by heating ground gypsum particles. After mixing with water, the mixture reverts to gypsum. This unique property of gypsum products has led to numerous applications throughout history. A mixture of plaster (a gypsum product), lime, and water was used in joining the stone blocks of ancient Egypt's pyramids. Gypsum and gypsum products are used widely in building construction, soil conditioning, food additives, pharmaceuticals, medical devices, and dental applications.

The primary applications of gypsum products in dentistry include the production of study models for oral and maxillofacial structures and use as auxiliary materials for dental laboratories involved in the production of dental prostheses. When refractory fillers are added, the gypsum product becomes more heat resistant and is known as a gypsum-based investment, capable of forming molds for the casting of alloys ([Chapter 14, Gypsum-Bonded Investments](#)).

CRITICAL QUESTION

Calcination is a process of removing the water of crystallization from the dihydrate. What happens if hemihydrate powder is mixed with water?

Production of Gypsum Products

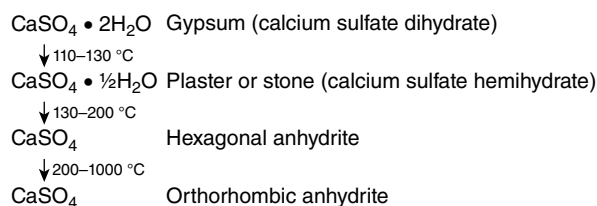
Gypsum products are produced by grinding the gypsum and subjecting it to temperatures of 110 to 130 °C in open containers to drive off part of the crystalline water ([Figure 13-19](#)). The principal constituent of gypsum products is calcium sulfate hemihydrate. The resulting particle is a fibrous aggregate of fine crystals with capillary pores ([Figure 13-20, A](#)) known as *plaster of Paris* or **dental plaster** in dentistry. As the temperature is further raised, plaster becomes hexagonal anhydrite and orthorhombic anhydrite. This process is known as *calcination*.

When gypsum is heated in a kettle, vat, or rotary kiln that maintains a moist environment, a crystalline hemihydrate called **dental stone** is produced ([Figure 13-20, B](#)). The powders are often referred to as α -hemihydrate for dental stone and β -hemihydrate for plaster of Paris.

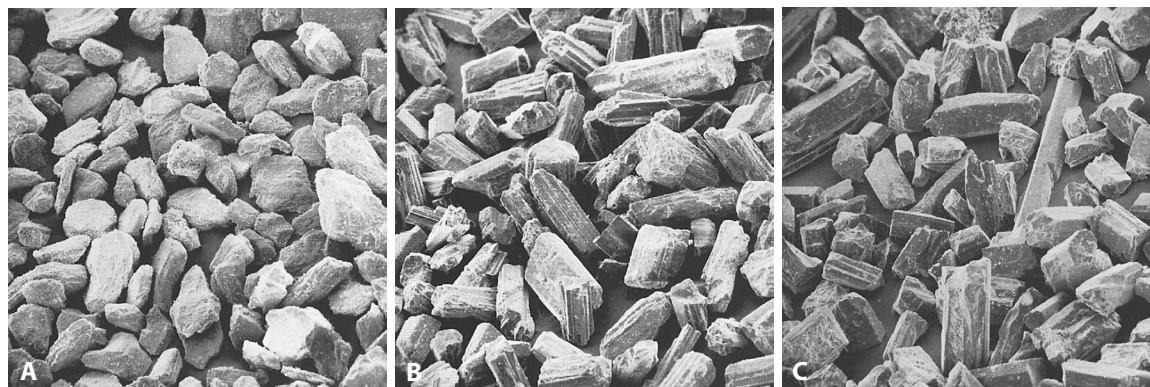
If the calcination process occurs under pressure in a 30% calcium chloride solution or in the presence of more than 1% of sodium succinate, the process yields shorter and thicker hemihydrate crystals called *modified α -hemihydrate* or die stone ([Figure 13-20, C](#)). Residual calcium chloride and sodium succinate are removed by washing the powder with hot water.

CRITICAL QUESTION

What is the mechanism of reverting calcium sulfate hemihydrate to dihydrate?



• **Figure 13-19** Calcination process for gypsum.



• **Figure 13-20** Three types of powder particles in gypsum-producing products (×400). **A**, Plaster of Paris (β -hemihydrate particles); crystals are spongy and irregular in shape. **B**, Dental stone (α -hemihydrate); crystals are prismatic and more regular in shape than those of plaster. **C**, Improved stone (modified α -hemihydrate); the cube-shaped particles have a reduced surface area that improves the flow of the mixture.

Setting of Gypsum Products

The reaction between gypsum products and water produces solid gypsum, and the heat evolved in the exothermic reaction is equivalent to the heat used originally for calcination. Set gypsum products probably never attain 100% conversion at room temperature.

Setting Reaction

There are three theories of gypsum setting. The colloidal theory proposes that, when mixed with water, hemihydrate enters the colloidal state through a sol–gel mechanism. In the sol state, hemihydrate particles are hydrated to form the dihydrate state. As the water added is consumed, the mass converts to a solid gel. The hydration theory suggests that sulfate groups in rehydrated plaster particles unite through hydrogen bonding with water to form the set material.

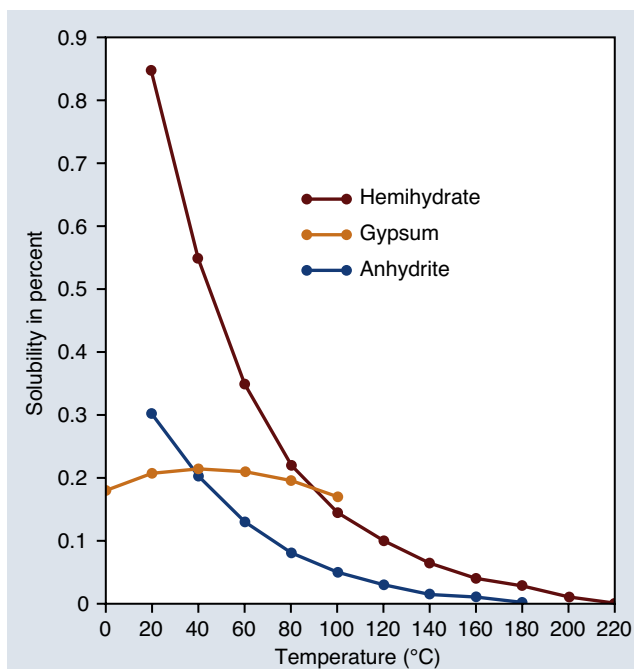
The most widely accepted theory is the dissolution–precipitation mechanism, which is based on the fact that the solubility of hemihydrate in water is greater than that of the dihydrate near room temperature (Figure 13-21). Thus the setting reactions occur as follows:

1. The hemihydrate particles form a fluid suspension after mixing in water.
2. The water becomes a saturated solution of Ca^{2+} and $(\text{SO}_4)^{2-}$ as the hemihydrate dissolves.
3. This saturated hemihydrate solution is a supersaturated solution with respect to the solubility of the dihydrate; precipitation of dihydrate occurs.
4. As the dihydrate precipitates, the hemihydrate continues to dissolve. The process continues until no further dihydrate can precipitate out of solution.

In reality, the setting is likely achieved by a combination of the three mechanisms.

CRITICAL QUESTION

How can one determine whether the hemihydrate and water mixture has set?



• **Figure 13-21** Temperature dependence of calcium sulfate solubility in water.

Quantifying Setting Reactions

The hemihydrate and water must be mixed uniformly and maintain a workable state to facilitate pouring of a **model** or the casting investment. The time from the addition of powder to the water until mixing is completed is called the *mixing time*, which takes 20 to 30 seconds via mechanical mixing or at least a minute of hand spatulation. The time from the start of mixing to the point when the consistency is no longer acceptable for the product's intended purpose is the *working time*. Generally, a 3-minute working time should allow sufficient time for mixing, pouring an impression and a spare impression, and cleaning the equipment before the gypsum becomes unworkable. As the reaction proceeds, the excess water on the surface is taken up in forming the dihydrate, so the mix loses surface gloss and gains strength. One must also recognize that the mixture needs to develop enough strength to resist fracture during the removal of the model from the impression. When the mix can resist penetration by a Gillmore needle, which has a tip that is 2.12 mm (1/12 inch) in diameter and weighs 113.4 g (¼ lb), the time elapsed is called the *initial setting time*. At this point, the mass still has no measurable compressive strength, and the cast cannot be safely removed from the impression. The elapsed time at which a heavier Gillmore needle, weighing 453.6 g (1 lb) and with a tip that is 1.06 mm (1/24 inch) in diameter, leaves only a barely perceptible mark on the surface is called the *final setting time*.

CRITICAL QUESTION

How can we control gypsum's setting rate?

Control of the Setting Time

There are three factors that control setting time:

1. Solubility of the hemihydrate—Increasing solubility of the hemihydrate achieves supersaturation of the dihydrate faster.
2. Number of nuclei of crystallization—The greater the number of nuclei of crystallization, the faster the dihydrate crystals will form.
3. Rate of crystal growth—Increasing or decreasing the rate of crystal growth will accelerate or retard the setting time.

In practice, these factors have been incorporated in the formulation of the material by the manufacturer and by manipulation techniques performed by the operator. For example, fine gypsum particle residues from incomplete calcination or addition by the manufacturer will shorten the setting time because of the increase in the number of nuclei.

The amounts of water and hemihydrate should be gauged accurately by weight. The weight (or volume) of the water divided by the weight of the hemihydrate powder is the W/P ratio. For example, if 100 g of dental stone is mixed with 28 mL of water, the W/P ratio is 0.28. This ratio is an important factor in determining the physical and mechanical properties of the final gypsum product. The use of a higher W/P ratio decreases the number of nuclei per unit volume, with a longer setting time.

During mixing, dihydrate crystals form and are broken into fine particles by the spatulation. These particles become nuclei of crystallization. Therefore, within practical limits, a longer and more rapid mixing of the gypsum will result in a shorter setting time.

Usually an increase in water temperature leads to an acceleration of a chemical setting reaction. Figure 13-21 shows that the difference in solubility between hemihydrate and gypsum becomes smaller with increasing temperature, and this condition lowers the

	$(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \longrightarrow 2 \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$		
Molecular mass (g)	290.28	54.05	344.33
Density (g/cm ³)	2.75	1.00	2.32
Equivalent volume (cm ³)	105.56	54.21	148.41
	$\frac{(105.56 + 54.21) - 148.41}{(105.56 + 54.21)} \times 100\% = 7.11\%$		

• **Figure 13-22** Volume changes from conversion of calcium sulfate hemihydrate to dihydrate.

driving force for forming the dihydrate; a temperature increase also results in a slower setting reaction. The decreased driving force causes the effect of temperature on the setting time to be erratic and to vary from one material to another.

CRITICAL QUESTION

What are the recommended methods to accelerate or retard the setting time for a given gypsum-forming product?

Modifiers for Controlling Setting Time

Chemical modifiers have been used extensively to increase or decrease the setting time of gypsum products; they are called *retarders* and *accelerators*, respectively. The manufacturers use both types of compounds to formulate gypsum products with specific setting times.

It has been observed that strong inorganic acids and their salts with strong or weak bases are accelerators. The most commonly used accelerator is potassium sulfate, which is particularly effective in concentrations up to 2%. Slurry water flowing out from a model trimmer contains numerous fine gypsum particles that act as nuclei of crystallization and are an effective accelerator. Stirring the slurry water before use is important to disperse these fine gypsum particles. Increasing the time or the speed of mixing can create more nuclei by crushing the developing dihydrate crystals into smaller particles, thereby accelerating the setting of the mix. At a concentration of 2% of the hemihydrate, sodium chloride is an accelerator. Sodium sulfate has its maximum acceleration effect at approximately 3.4%. Several inorganic salts play dual roles in the setting kinetics of dihydrate, which are accelerators at low concentration and retarders at higher concentration. For example, borax, a known retarder for gypsum setting, has also been shown to promote the growth of dihydrate crystals, but only at a concentration lower than 0.2 mM (about 0.08 g/L).

One should recognize that significant acceleration of the reaction time could compromise the optimal flow characteristics of the material. The manufacturer has added accelerators, retarders, and other controlling agents, so adding other ingredients that may counteract the effects of components that are already incorporated into the product is not wise. Therefore one should select a product from the manufacturer's catalog with the specific setting time that the operator needs.

CRITICAL QUESTION

When a mixture of hemihydrate and water sets, the resulting object is always porous. Why?

Setting Expansion

Regardless of the type of gypsum product selected, an expansion of the mass can be detected during the formation dihydrate. The observed linear expansion may be as low as 0.06% or as high as

0.5%. This phenomenon is contrary to what is expected when hemihydrate reverts to the denser dihydrate form. If equivalent volumes of the hemihydrate, water, and the reaction product (dihydrate) are compared, the volume of the dihydrate formed will be 7.11% less than the equivalent combined volumes of the hemihydrate and water ([Figure 13-22](#)). The phenomenon of *setting expansion* can be explained based on crystallization.

Mechanism of Setting Expansion

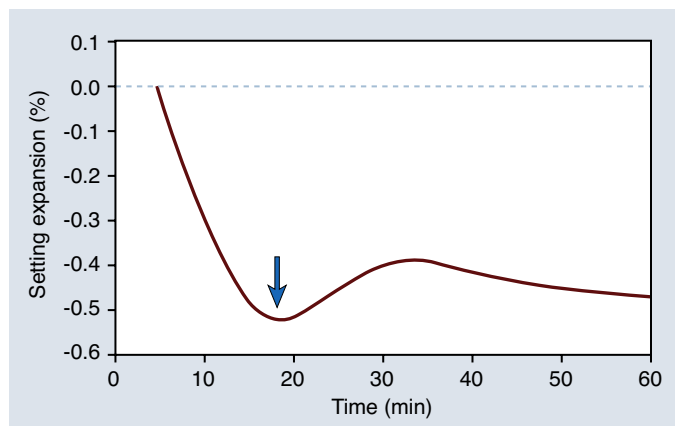
The crystallization of dihydrates can be pictured as an outgrowth of crystals from nuclei of crystallization. Crystals growing from the nuclei can intermesh with and obstruct the growth of adjacent crystals. When the process repeats itself with thousands of the crystals during growth, an outward stress or thrust results in an expansion of the entire mass. Thus a setting expansion can take place even though the true volume of the crystals alone may be less than calculated. Therefore the structure immediately after setting is composed of interlocking crystals, between which are micropores and pores containing the excess water required for mixing. On drying, the excess water is lost, resulting in a porous structure.

[Figure 13-23](#) shows the dimensional change during the setting of a gypsum product. The mixture exhibits an initial contraction followed by an expansion and smaller contraction. The initial contraction is caused by the surface tension of water pulling the particles closer. When the mixture is poured into an impression, the gypsum may continue contracting during the induction period. That contraction is of no concern because the mixture still flows and adapts to the impression. Only when the mixture is sufficiently rigid (after the initial set) will the force of expansion produce a visible setting expansion of the cast.

It is important to note that only the setting expansion that occurs after the initial set is of interest. When enough crystals have formed to produce the outward thrust by impingement, setting expansion follows. The onset of the initial setting occurs at approximately the minimal point of the curve, the point at which expansion begins. Because the contraction prior to the initial setting occurs at the free surface, the final dimension of the cast relative to that of the impression mold includes a setting expansion of approximately 0.12%, according to [Figure 13-23](#). Naturally, the quantities of setting expansion vary among different gypsum products.

Control of Setting Expansion

As can be noted from the results presented in [Table 13-9](#), a lower W/P ratio and a longer mixing time will increase the setting expansion. Each of these factors increases the nuclei density. The effect of the W/P ratio on the setting expansion is to be expected on theoretical grounds. At higher W/P ratios, fewer nuclei of crystallization per unit volume are present compared with the greater density of nuclei in thicker mixes. Because it can be assumed that the space between the nuclei is greater in such a case, it follows that there is less growth interaction of the dihydrate crystals and less outward thrust. However, the most effective method by which



• **Figure 13-23** Dimensional changes that occur during the setting of a gypsum product. The arrow indicates the initial set at approximately the lowest point of the curve.

TABLE 13-9 Effect of Water/Powder (W/P) Ratio and Mixing Time on Setting Expansion of Plaster of Paris

W/P Ratio	Mixing Time (min)	Setting Expansion (%)
0.45	0.6	0.41
0.45	1.0	0.51
0.60	1.0	0.29
0.60	2.0	0.41
0.80	1.0	0.24

From Gibson CS, Johnson RN: Investigations of the setting of plaster of Paris, *J Soc Chem Ind* 51(1):25T, 1932.

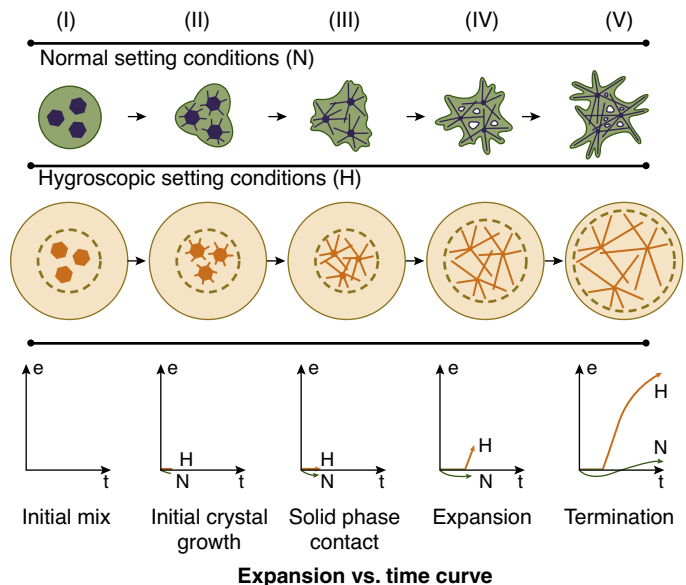
to control setting expansion is through the addition of chemicals by the manufacturer.

CRITICAL QUESTION

Thus far, the setting of plaster or stone has occurred in air. What would happen if the hemihydrate and water mixture could set underwater? Keep in mind that the solubilities of hemihydrate and dihydrate are very low in water, and one should not be concerned that the mixture will dissolve without vigorous stirring.

Hygroscopic Setting Expansion

Imagine that the initial mix is represented in the top row of Figure 13-24 (stage I) by the three round particles of hemihydrate surrounded by water. Under normal setting conditions, the crystals of the dihydrate begin to form on the nuclei. The water around the particles is reduced by hydration, and these particles are drawn more closely together because the surface tension of the water keeps the water surface area at a minimum (stage II). As the crystals of dihydrate grow, they contact each other, and the water around the particles again decreases (stage III). Further dihydrate growth consumes more water and should draw the crystals together as before, but the outward thrust of the growing crystals opposes this contraction (stage IV). Eventually, the crystals become intermeshed and entangled (stage V).



• **Figure 13-24** Diagrammatic representation of the setting expansion of gypsum products. In the top row, the crystal growth is inhibited by the surface tension of water surrounding the growing crystals. In the middle row, the gypsum mixture (the area surrounded by the dashed circle) is immersed in water during setting (represented by the larger solid circle); the immersion water provides more room for longer crystal growth. The bottom row shows the expansion (e) over time (t) for hygroscopic setting expansion (H) and normal setting expansion (N). (Adapted from Mahler DB, Ady AB: An explanation for the hygroscopic setting expansion of dental gypsum products, *J Dent Res* 39:378–379, 1960.)

Stage I of the middle row (hygroscopic setting conditions) of Figure 13-24 shows an identical mixture of hemihydrate (the area delineated by the dashed circle) underwater (the area outside of the dashed circle). The hydration of hemihydrate particles here would proceed as usual. Because they are surrounded by a body of water, the surface tension of water will not be pulling or pushing these growing crystals (stage II). As the dihydrate crystals continue to grow and contact each other, no reduction in the distance between crystals is expected (stage III). This means that the crystals will grow much more freely during the early stages (stage IV) before the intermeshing finally prevents further expansion (stage V). Consequently, the observed setting expansion that occurs when the gypsum product sets underwater is greater than that which occurs during setting in air.

To distinguish between the two setting conditions, the setting expansion without water immersion is usually called **normal setting expansion** (N in the bottom row of Figure 13-24), whereas the expansion that occurs underwater is known as **hygroscopic setting expansion** (H in the bottom row of Figure 13-24).

The hygroscopic expansion obtained during the setting of dental stone or plaster is about twice that of the normal setting expansion. This property has been used in the formulation of investment materials to compensate for the casting shrinkage. More discussion on the hygroscopic expansion of investment materials is presented in Chapter 14, **Hygroscopic Setting Expansion**.

Note that *hygroscopy* means the ability of a substance to attract water molecules from the surrounding environment through either absorption or adsorption. The hygroscopic setting expansion described here is not the result of absorption or adsorption. Therefore the term *hygroscopic setting expansion*

of gypsum products is technically incorrect. Nonetheless, this term is retained in explanations of the setting expansion of gypsum.

CRITICAL QUESTION

How does the presence of water in the pores of set gypsum affect the strength of the gypsum object?

Strength of Set Gypsum Products

The strength of set gypsum products as a brittle material is generally expressed in terms of compressive strength.

Effect of Water Content

The free water content of the set product affects product strength. For this reason, two strength properties of gypsum are reported: the *wet strength* (also known as *green strength*) and the *dry strength*. The wet strength is the strength that is determined when water in excess of that required for hydration of the hemihydrate remains in the test specimen. When such excess water is removed by drying, the strength obtained is the dry strength. The dry strength may be two or more times as high as the wet strength.

The effect of drying period on the compressive strength of set plaster is shown in Table 13-10. Note the relatively slight gain in strength that occurred after 8 hours of drying and the loss of water. Between an 8-hour and a 24-hour drying period, only 0.6% of the excess water was lost, yet the strength doubled. A similar change in surface hardness takes place during the drying process. Keep in mind that the excess water in the set gypsum products is saturated with Ca^{2+} and SO_4^{2-} . As the last trace of water is lost, fine crystals of gypsum precipitate serve as anchors between the larger crystals. Thus, if excess water is reconstituted by immersion or absorption, these small crystals are the first to dissolve, and the reinforcing anchors are lost.

Microwave irradiation has been used to speed up the drying and disinfection of gypsum casts. The influence on the strength of the gypsum cast, however, is inconclusive. In general, microwave irradiation, a timesaving procedure, may be associated with some dimensional changes. The time needed varies with the microwave oven setting and the type of cast being dried.

TABLE 13-10 Effect of Drying Period on the Strength of Plaster of Paris

Drying Period (h)	Compressive Strength (MPa)	Weight Loss (%)
2	9.6	5.1
4	11.7	11.9
8	11.7	17.4
16	13.0	—
24	23.3	18.0
48	23.3	18.0
72	23.3	—

From Gibson CS, Johnson RN: Investigations of setting of plaster of Paris, *J Soc Chem Ind* 51(1):25–38, 1932.

Effect of Water/Powder Ratio

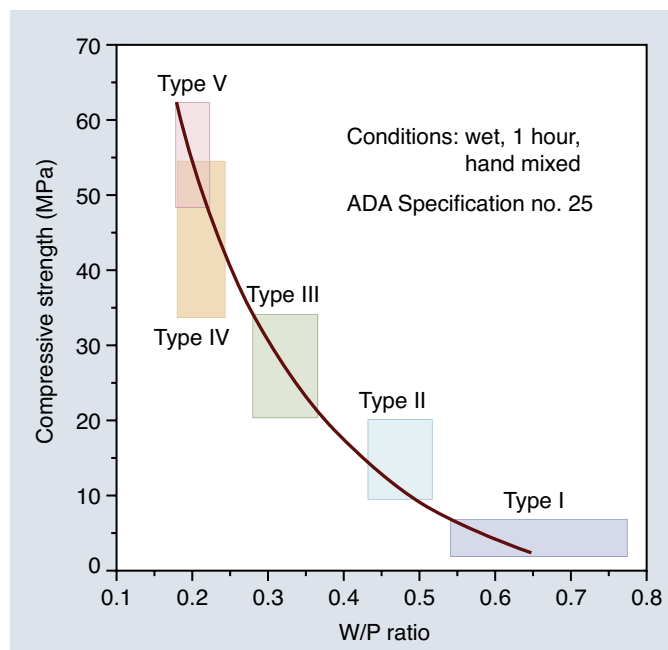
As previously noted, the set plaster or stone is porous, and the greater the W/P ratio, the greater the porosity. As might be expected on such a basis, the greater is the W/P ratio, the less is the strength of the set material, as shown by the data in Table 13-11, because fewer dihydrate crystals are available per unit volume.

Figure 13-25 is a plot of the strength as a function of the W/P ratio for the five different types of gypsum products used in dentistry (discussed later). The figure includes data from many of the products on the market that meet ANSI/ADA Specification No. 25 or ISO 6873 for dental gypsum products (Table 13-12). The compression test was conducted 1 hour after the start of mixing; therefore the values obtained are wet strength of the materials tested. Although the W/P ratio varies for the brand of plaster or stone, the typical recommended ranges of W/P ratios are shown in Table 13-12 for the five types of gypsum products.

TABLE 13-11 Effect of the Water/Powder (W/P) Ratio and Mixing Time on the Strength of Plaster of Paris

W/P Ratio	Mixing Time (min)	Compressive Strength (MPa)
0.45	0.5	23.4
0.45	1.0	26.2
0.60	1.0	17.9
0.60	2.0	13.8
0.80	1.0	11.0

From Gibson CS, Johnson RN: Investigations of setting of plaster of Paris, *J Soc Chem Ind* 51(1):25T, 1932.



• **Figure 13-25** One-hour compressive strength as a function of water/powder (W/P) ratio for five types of gypsum products. ADA, American Dental Association.

TABLE 13-12 Typical W/P Ratios and Properties Requirements of Gypsum Products

Type	W/P Ratio	Setting Time* (min)	2-h Setting Expansion* (%)	1-h Compressive Strength* (MPa)
I. Plaster, impression	0.50–0.75	2.5–5.0	0.0–0.15	4.0 [§] –8.0 [†]
II. Plaster, model	0.45–0.50	TBD	0.0–0.30	9.0 [§]
III. Dental stone	0.28–0.30	TBD	0.0–0.20	20.0 [§]
IV. Dental stone, high strength	0.22–0.24	TBD	0.0–0.15	35.0 [§]
V. Dental stone, high strength, high expansion	0.18–0.22	TBD	0.16–0.30	35.0 [§]

TBD—The setting time should be within 20% of the value claimed by manufacturer.

*Property requirements specified in ANSI/ADA Specification No. 25 and ISO 6873:2013.

[§]Minimum strength value.

[†]Maximum strength value.

Effect of Manipulation and Additives

As shown in Table 13-11, the mixing time also affects the strength of the plaster. In general, an increase in mixing time increases the strength to a limit. If the mixture is overmixed, the gypsum crystals will be broken up, and the final product will hold less crystal-line interlocking structure.

The addition of an accelerator or retarder lowers both the wet strength and the dry strength of the gypsum product. Such a decrease in strength can be partially attributed to the salt added as an adulterant and to the reduction in intercrystalline cohesion.

When relatively pure hemihydrate is mixed with minimal amounts of water, the working time is short, and the setting expansion is unduly high. However, as just noted, dental gypsum products contain additives that reduce the setting expansion, increase the working time, and provide a rapid final set. The addition of more chemicals can upset the delicate balance of these properties. Thus, if a change is desired in the setting time, this should be controlled by modest alterations in the W/P ratio and/or the spatulation time.

CRITICAL QUESTION

Which properties are used to classify the various types of gypsum products?

Types of Gypsum Products

ANSI/ADA Specification No. 25 classifies five types of gypsum products and gives the property requirements for each type (Table 13-12). Some gypsum materials are formulated for special purposes, such as for pouring orthodontic casts or attaching casts to an articulator. The criterion for selecting any gypsum product depends on the intended use and the physical properties necessary for that particular use.

Impression Plaster (Type I)

These impression materials are composed of plaster of Paris to which modifiers have been added to regulate the setting time and setting expansion. Impression plaster is now rarely used for making dental impressions because plaster has been replaced by less rigid materials such as the hydrocolloids and elastomers. Descriptions of the impression plaster and applications were given earlier.

Model Plaster (Type II)

Model plaster or laboratory type II plaster is now used principally to fill a flask used in denture construction when setting expansion is not critical and the strength is adequate according to the limits cited in the ADA specification or ISO standard. It is usually marketed in the natural white color, thus contrasting with stones, which are generally colored.

Dental Stone (Type III)

Type III stone has a minimal 1-hour compressive strength of 20.0 MPa. It is intended for the construction of casts in the fabrication of full dentures to fit soft tissues. For this application, a slight setting expansion can be tolerated in casts that reproduce soft tissues, but not when teeth are involved. Type III stones are preferred for casts used to process dentures because the stone has enough strength for this purpose but low enough strength for separating the denture from the cast.

There are at least two methods for the construction of the cast. One method is to construct a mold by wrapping soft flat wax strips around the impression so that they extend approximately 12 mm beyond the tissue side of the impression. This process is called *boxing*, which forms the base of the cast. The mixture of stone and water is then poured into the impression under vibration. Another method is to fill the impression first as described but without wrapping. The remainder of the stone–water mixture is poured on a glass plate. The filled impression is then inverted over a mound of stone, and the base is shaped with the spatula before the stone sets. Such a procedure is not indicated if the impression can easily be deformed or if the stone is “runny.” The cast should not be separated from the impression until the stone has hardened. The minimal time allowed for setting varies from 45 to 60 minutes, depending on the rate of setting of the stone or plaster and the type of impression material used.

Dental Stone, High Strength (Type IV)

The principal requisites for a die material are strength, hardness, and minimal setting expansion. To obtain these properties, modified α -hemihydrate, also called *die stone*, is used.

A hard surface is necessary for a die stone because the tooth preparation is covered with wax and carved flush with the margins of the die. A sharp instrument is used for this purpose; therefore the stone must be resistant to abrasion. Gypsum hardening

solutions, silver plating, coating with cyanoacrylate adhesive, and other methods of increasing the abrasion resistance are discussed in [Chapter 14, Preparation of the Master Die](#). It is fortunate that the surface hardness increases more rapidly than the compressive strength because the surface dries more rapidly. This is a real advantage in that the surface resists abrasion, whereas the core of the die is tough and less subject to accidental breakage. The average dry surface hardness of the type IV stones is approximately 92 (Rockwell hardness), and that of type III stone is 82. Even though the surface of the type IV stone is harder, care should be taken when the pattern is being carved.

CRITICAL QUESTION

Under what conditions might a type V dental stone be used?

Dental Stone, High Strength, High Expansion (Type V)

This gypsum product exhibits an even higher compressive strength than the type IV dental stone. The improved strength is attained by lowering the W/P ratio even further than that used for type IV stone. In addition, the setting expansion has been increased from a maximum of 0.16% to 0.30% ([Table 13-12](#)). The rationale for increasing the setting expansion is the use of base metals that have a greater casting shrinkage than do the traditional noble-metal alloys ([Chapter 9, Alternative Technologies for Fabricating Prostheses](#)). Thus higher expansion is required in the stone die to aid in compensating for the alloy solidification shrinkage. The use of a type V stone may also be indicated when the expansion achieved during the fabrication of cast crowns is inadequate. One should avoid the use of type V stones for producing dies for inlays and onlays because the higher expansion may lead to an unacceptably tight fit.

Special Gypsum Products

The orthodontist prefers a white stone or plaster for study models and may treat the surface with soap to acquire sheen. These products generally have a longer working time that reduces void formation and facilitates trimming.

Mounting casts to articulators requires a gypsum product, which is referred to as “mounting” stone or plaster. These products are fast setting and exhibit low setting expansion. In addition, they have a sufficiently low strength, permitting easy trimming and facilitating separation of casts from the articulator mounting plates.

Some products are designed to save time. One type is extremely fast setting and is ready to use in 5 minutes, but it has little working time. Another product changes color to indicate when it is ready for use. In addition, one specialty product contains a small amount of plastic or resin to reduce brittleness and improve resistance to abrasion during the carving of wax patterns.

Manipulation of Gypsum Products

In practice, clinicians and technicians must not only produce a cast using a gypsum-producing material, but they must also store the powder properly and maintain the cast in the best condition for subsequent procedures.

Care of Gypsum Products

If the relative humidity of the surroundings exceeds 70%, the plaster absorbs sufficient moisture from the air to start a setting reaction. The initial hydration probably produces a few dihydrate crystals on the surface of the exposed hemihydrate particles.

These dihydrate crystals can act as nuclei of crystallization and accelerate the setting when the powder is mixed with water. If the hydration continues during storage, hemihydrate crystals could become completely covered with dihydrate crystals. Under these conditions, the water penetrates the dihydrate coating with difficulty, and the setting time is prolonged. The best means of storage is to seal the product in a moisture-proof metal container.

Proportioning

The measurement should be made with a graduated cylinder for water by volume and a weighing balance for the weight of powder. Measurement of powder by volume is not reliable because of non-uniform powder packing. Prew weighed envelopes are very popular because they promote accuracy, reduce waste, and save time.

Mixing and Pouring

If mixing is performed by hand, the bowl should be parabolic in shape, smooth, and resistant to abrasion. The spatula should have a stiff blade and a handle that is convenient to hold. A measured amount of water is placed in the bowl first, followed by sifting the weighed powder into the water as initial hand mixing is performed. The mixture is then vigorously stirred, with periodic wiping of the inside of the bowl with the spatula to ensure wetting of all the powder and breaking up of any agglomerates or lumps. The mixing should continue until a smooth mix is obtained, usually within a minute. A longer spatulation time drastically reduces the working time. The use of a vibrator of high frequency and low amplitude to reduce air entrapment is essential before pouring.

The preferred method of mixing is to use a mechanical mixer under vacuum. First, the measured water is added to the bowl, followed by gradual addition of the preweighed powder. The powder is incorporated during approximately 15 seconds of mixing with a hand spatula, followed by 20 to 30 seconds of mechanical mixing under vacuum. The strength and hardness obtained from such vacuum mixing usually exceed that obtained by hand mixing.

Before pouring, the mixing bowl with the dental stone mixture should be vibrated to eliminate more entrapped air and set aside. The impression tray is held in one hand against the vibrator. The surface of the impression should be free of excess water. When tooth preparations are involved, a small spatula about the size of the preparation may be used to deliver enough stone to fill all preparations. The speed of the vibrator should be adjusted high enough to make the stone flow slowly into the space. After the preparation and the anterior teeth are filled, more dental stone can be added from one open end of the impression (e.g., in the last molar of a full-arch impression). The impression may be tilted to facilitate the movement of the stone into the tooth depression. Additional stone is added behind the moving front to promote the flow of stone and to ensure that the previously filled area does not lose much of its volume. Once the tooth depressions are filled, larger amounts of dental stone can be added under light vibration to fill the remaining impression up to the mucobuccal fold or rim of the boxed area around the impression tray. The impression is then briefly placed on the vibrator for a few seconds to distribute the stone evenly across the impression.

If the inversion method is used, a mound of stone about 20 mm high is made on a flat surface, such as a glass plate, with the remainder of the mixture or with a new mix using a lower W/P ratio. The stone in the filled impression should exhibit the initial set but not the final set before the impression is then inverted over the mound of stone. The base is shaped with the spatula, and the entire assembly is left undisturbed until the material has set completely. The dental stone model is then separated from the impression.

CRITICAL QUESTION

What storage conditions are necessary to maintain the dimensional accuracy of a gypsum cast?

Care of the Cast

The cast dimensions should be relatively constant under ordinary conditions of room temperature and humidity. However, soaking casts in water may be necessary in preparation for other procedures. A study has reported that a stone cast immersed in a container under running water will lose approximately 0.1% of the cast's linear dimension for every 20 minutes of immersion. Therefore the safest method for soaking the cast is to place the cast in a water bath with gypsum debris remaining on the bottom of the container to provide a saturated solution of calcium sulfate.

CRITICAL QUESTION

What procedure should be followed if it is uncertain whether the impression or the gypsum cast has been disinfected?

Infection Control

Concern over possible cross-contamination of dental office personnel by microorganisms, including hepatitis B virus and human immunodeficiency virus, via dental impressions has prompted study of the effect of spray- and immersion-disinfecting techniques on impression materials. The effect of such agents on the surface quality and accuracy of the resulting gypsum casts is an important consideration.

If an impression has not been disinfected or if the laboratory had no assurance that an appropriate disinfection protocol was followed, disinfecting the stone cast will be necessary. Disinfection solutions can be used that do not adversely affect the quality of the gypsum cast. Alternatively, disinfectants can either be incorporated in the powder or dissolved in the mixing water. The addition of a disinfectant in the gypsum products would undoubtedly influence some of the properties of certain products, such as strength, setting expansion, and setting time. The precise effect depends on the types of gypsum and antimicrobial agents used. Nonetheless, the disinfected stones apparently compare favorably with nondisinfected controls.

The same microwave irradiation used in drying gypsum casts has also been evaluated in infection control. One study showed that a 5-minute irradiation at 900 W reduced microorganism counts (cfu/mL), with a median log value of 6 to median counts (cfu/mL) of zero. Data on the effectiveness of microwave irradiation on different microorganism species, based on the power setting, the duration needed, and the influence of prolonged irradiation on the properties of the gypsum cast, are not available.

The widespread availability of a spectrum of disinfected dental stone casts (type III to type V) with proven efficacy and unimpaired physical properties will undoubtedly strengthen the barrier system of infection control in the dental laboratory.

Dental Waxes

Wax is a thermoplastic polymer that can be molded with or without a slightly elevated temperature and retain the new shape when cooled to room temperature. The fabrication of fixed and removable dental prostheses uses various forms of wax during clinical procedures or processing in the laboratory. Clinical products include bite registration wax, disclosing wax (pressure-indicating paste), utility waxes for altering and adapting impression trays, and waxes for making wax patterns. Laboratory products include

boxing wax, baseplate wax, sticky wax, beading wax, utility wax, and waxes for making pattern prostheses on patients' models.

Waxes for dental procedures are a blend of natural and synthetic waxes. Natural waxes are taken from plants, insects, animals, or minerals (including petroleum); synthetic waxes are made by the synthesis of polymers or the modification of natural waxes. Mineral-based waxes are mostly mixtures of hydrocarbons, whereas waxes from plants, insects, and animals contain hydrocarbons with ester and some with alcohol or acid. Synthetic waxes are typically composed of hydrogen, carbon, oxygen, and chlorine. Synthetic waxes are more uniform than natural waxes in their structure and more homogeneous in composition.

Components of Dental Waxes

Blending natural and synthetic waxes along with other additives creates unique working characteristics for the intended applications. For example, coloring agents are added to provide a contrast of wax patterns against the hues of teeth, dies, and model surfaces. Ivory-colored wax is useful for aesthetic case presentations to patients. Fillers can be added to control expansion and shrinkage of the wax product. Some major components of **dental waxes** are discussed next.

Paraffin, derived from fractions of petroleum, is a colorless or white, somewhat translucent hard wax with a wide range of melting or softening temperatures. Paraffin wax flakes when trimmed and does not produce a smooth, glossy surface. *Microcrystalline* wax, derived from heavier petroleum fractions, has a higher melting point, crystallizes in small plates, and is tougher and more flexible than paraffin waxes. *Gum dammar*, a natural resin, improves the smoothness in the molding of paraffin-based wax and renders the wax resistant to cracking and flaking. *Carnauba wax*, a very hard wax with an agreeable odor from carnauba palm trees, has a relatively high melting point that decreases the **flow** of the paraffin at mouth temperature and improves the glossiness of the wax surface.

Certain synthetic waxes can be used in place of carnauba wax. They include a nitrogen derivative of the higher fatty acids or esters of acids derived from *Montan wax*. *Candelilla wax* is a plant-based wax that has the same effect as carnauba wax with a lower melting point. *Ceresin* is extracted from ozokerite, a waxy mineral mixture with a somewhat unpleasant odor. Ceresin may replace part of the paraffin to modify the toughness and carving characteristics of the wax.

Types of Dental Waxes

Dental waxes can be classified into one of three types by the application: pattern wax, processing wax, and impression wax. In this section, we discuss relevant properties critical to the intended applications.

Pattern Wax

Pattern waxes are used to form the outline of a prosthesis, which is to be constructed of a more durable material such as cast alloys, hot-isostatically pressed ceramics, or compression molded resins. They include **inlay wax**, casting wax, and baseplate wax.

Inlay waxes may be softened over a flame or in water at 54 to 60 °C to enable their flow in the liquid state and their adaptation to the prepared tooth (direct technique that is no longer common) or die (indirect technique). Type I is a direct technique wax, and type II is an indirect technique wax (ANSI/ADA Specification No. 4 [1983]). Before the adaptation of the pattern wax within a tooth or a die, a separating medium must be used to ensure the complete separation of the wax pattern without distortion.

Dipping wax, which is kept molten during the process, can be used to facilitate the wax-pattern preparation. A well-lubricated die is

immersed in this wax briefly, and the wax coating is uniform in thickness when cooled to room temperature. After the pattern is removed from the prepared cavity, the pattern is encased in a gypsum- or phosphate-based material or other type of **refractory** material known as an investment. The role of the investment in obtaining a casting that fits the preparation is discussed in [Chapter 14, Investment Materials](#).

Because of the extremely high thermal expansion coefficient value compared with those for other dental materials, the type I inlay wax will shrink appreciably as it is cooled to room temperature. A pattern made by the indirect method may not shrink as much, although the amount depends on whether the pattern has reached room temperature before it is removed from the die.

Casting waxes serve the same purpose as inlay wax but are used to make patterns for the metallic framework of removable partial dentures and other similar structures that include sculpting and buildup. They come in sheets, pearls, and a variety of ready-made forms, such as round, half-round, and half-pear-shaped rods and wires of various gauges. Most casting waxes contain no synthetic material and have more high-molecular-weight molecules; this allows the wax to have excellent sculpting characteristics, quick cooling down, and the ability to remain opaque even in the molten state to lend better control during wax-up.

Baseplate wax is used to establish the initial arch form in the construction of complete dentures. Supplied in 1- to 2-mm-thick red or pink sheets, they come in three types for specific applications. Type I, a soft wax, is used for building contours and veneers. Type II, a medium wax, is designed for pattern production in the mouth in normal climatic conditions. Type III, a hard wax, is used for trial fitting in the mouth in tropical climates (ANSI/ADA Specification No. 24 [1991: Reaffirmed 2003]). The classifications of baseplate wax described in ISO 15854:2021 are Type 2/Class 1: Soft, Type 2/Class 2: Hard, and Type 2/Class 3: Extra hard. Because residual stress is present within the wax from contouring and manipulating the wax, the finished denture pattern should be flaked as soon as possible after the completion of all adjustments and manipulations.

Processing Wax

The role of processing waxes is primarily in simplifying the dental procedures for constructing a variety of devices and appliances, in the clinics or in the laboratory.

Utility wax is a moldable wax that can adhere to various dry surfaces when pressed on. This wax transforms a standard perforated impression tray for use with hydrocolloids into a more desirable contour and protects soft tissue from the periphery to extend or post dam impression trays. Utility wax can be used to repair small imperfections in wax patterns, to fill holes, or to apply **sprues** to sprue bases ([Chapter 14, Sprue Position and Attachment](#)).

Sticky wax is an orange-colored wax in the form of stick, which is tacky when melted but firm and brittle when cooled. Sticky waxes are used to temporarily fasten gypsum model components, join and temporarily stabilize the components of a bridge before soldering, or attach pieces of a broken denture prior to a repair.

Boxing wax is intended for enclosing an impression before a stone cast is poured. Typically provided in pink-colored flat sheets, this wax is relatively soft and pliable and can easily be pressed to the desired contour around the perimeter of an impression and self-sealed at the overlapped area with firm pressure.

Impression Wax

The impression waxes, also referred to as **bite waxes** or **corrective waxes**, tend to distort if they are withdrawn from undercut areas. Thus they are limited to use in edentulous sites of the mouth or in

occlusal surface areas. Nonetheless, they have enough body to register the detail of soft tissues, and they are rigid at room temperature.

Properties of Wax

Of the three types of waxes discussed, the sensitivity of the wax to the surrounding environment and the intrinsic properties is critical to the application of pattern waxes. Therefore the properties discussed in this section address the requirements of pattern waxes. The desired properties of pattern waxes are as follows:

1. The wax should be uniform when softened.
2. The color should contrast with die materials or prepared teeth to facilitate proper finishing of the margins.
3. The wax should not fragment into flakes or similar surface particles during carving after cooling.
4. The wax must not be pulled away by the instrument or chip during carving.
5. During the burnout phase, the wax must burn completely by oxidizing residual carbon to volatile gases. Ideally, the wax should not leave a solid residue that amounts to more than 0.10% of the original weight of the specimen after the burnout phase.

Flow of Dental Wax

Flow, by definition, is a measure of the degree of permanent deformation of the material at a given temperature below the melting temperature of the wax. We use type I inlay wax to discuss the significance of flow property. When a wax pattern is to be made with type I inlay wax, the wax must have a relatively high flow a few degrees above mouth temperature so that the wax is workable but not uncomfortably warm when placed in the mouth of the patient. At mouth temperature, the same wax must have essentially no flow to minimize the possibility of distortion of the pattern during removal from the tooth preparation. The temperature–time cooling curve of a paraffin-based inlay wax ([Figure 13-26](#)) features two inflections; the upper one indicates hardening of the wax below 65 °C and becoming solid below around 48 °C. They do not show the precise melting range of the wax but indicate the successive solidification of progressively lower-molecular-weight fractions. This condition promotes moldability of the wax.

Flow is measured by subjecting cylindrical specimens to a designated load at the stated temperature and measuring the percentage of reduction in height. Requirements for the flow properties of inlay waxes at specific temperatures are summarized in [Table 13-13](#). The low flow value at 37 °C permits carving and removal of the pattern from the prepared cavity at mouth temperature without distortion. A flow range of 70% to 90% for type I and type II inlay waxes at 45 °C facilitates flow into all areas in the preparation and reproduction of details on the wax pattern.

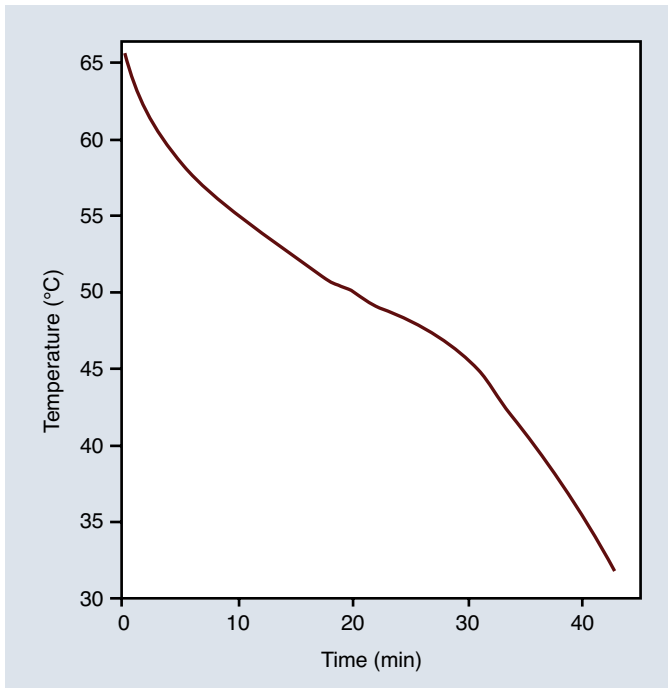
Thermal Properties of Dental Waxes

Waxes are softened with heat, forced on the prepared tooth or the die, and cooled. The thermal conductivity of the waxes is low, and sufficient time must be allowed both to heat them uniformly throughout and to cool them to body or room temperature, as with impression compounds. Another thermal characteristic of wax is its high coefficient of thermal expansion. As shown in [Figure 13-27](#), the inlay wax may expand as much as 0.7% with a 20 °C increase in temperature or contract as much as 0.35% when it is cooled from 37 to 25 °C. The effect of low thermal conductivity and high thermal contraction is less significant when the wax is used in the indirect technique because the pattern is not subjected to a change from mouth to room temperature.

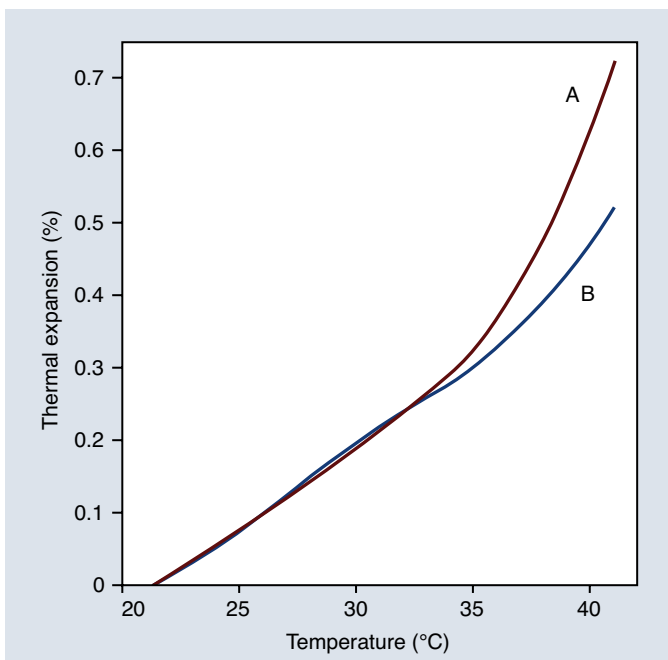
The thermal dimensional change may be affected by the previous manipulation of the wax. [Figure 13-27](#) shows the thermal

TABLE 13-13 Requirements for Inlay Casting Wax Flow (%)

Type of Wax							
ANSI/ADA Spec. No. 4 (1983; Reaffirmed 2003)	ISO 15854:2021	T = 30 °C		T = 37 °C		T = 40 °C	
		Max.		Max.		Min.	Max.
Type I	Type 1, Class 2	—		1.0		—	20.0
Type II	Type 1, Class 1	1.0		—		50.0	—
						70.0	90.0



• **Figure 13-26** Time-temperature cooling curve for type I inlay wax.



• **Figure 13-27** Thermal expansion of inlay wax. Curve A represents the thermal expansion when the wax was held under pressure while it was cooling from the liquid state. When the same wax is cooled without pressure and heated again, the behavior shown by curve B occurs.

expansion of two wax specimens as a function of temperature; curve A is the specimen that has previously cooled under pressure, whereas curve B is the specimen that cooled free of pressure. Both curves show a greater expansion rate above 35 °C. Recall from the discussion in [Chapter 2, Thermal Properties](#), that the temperature where this characteristic change occurs is known as the *glass-transition temperature* ([Figure 2-28](#)). The deviation between the two curves occurs because specimen A had yielded more crystalline structure under pressure that exhibits a greater rate of expansion while passing through the glass-transition zone.

CRITICAL QUESTION

How can one best minimize the potential distortion effects associated with elastic memory and temperature changes?

Mechanical Properties

The weak intermolecular bonds of dental waxes that afford the dental profession all the ease of manipulation and convenience of the intended applications also yield a material of low elastic modulus and associated mechanical properties that are sensitive to temperature compared with those of other dental materials. This is a major limitation of wax.

Residual Stress and Wax Distortion

Distortion of wax patterns can occur when forming and removing the pattern from a tooth or die. Distortion of a wax pattern can result from occluded air in the pattern, physical deformation (during molding, carving, or removal), release of stresses “trapped” during previous cooling, excessive storage time, and extreme temperature changes during storage.

Because of low thermal conductivity, the outer layer of the wax cools first while the core remains in a liquid state and continues to contract. When the core finally cools to a solid, the contraction process is constrained by the already-solid external layers, resulting in residual stress. A newly made wax pattern not retained on the die tends to change its shape over time, a sign of stress relieving to reach a state of dimensional stability. Thus it is important that the wax pattern be retained on the die for several hours to avoid distortion and ensure that equilibrium conditions are established.

A casting will fit most accurately when the pattern is invested immediately after its removal from the preparation or the die. Any delay in investing the pattern can lead to a distortion of its form because of stress-relaxation effects.

Manipulation of Inlay Wax

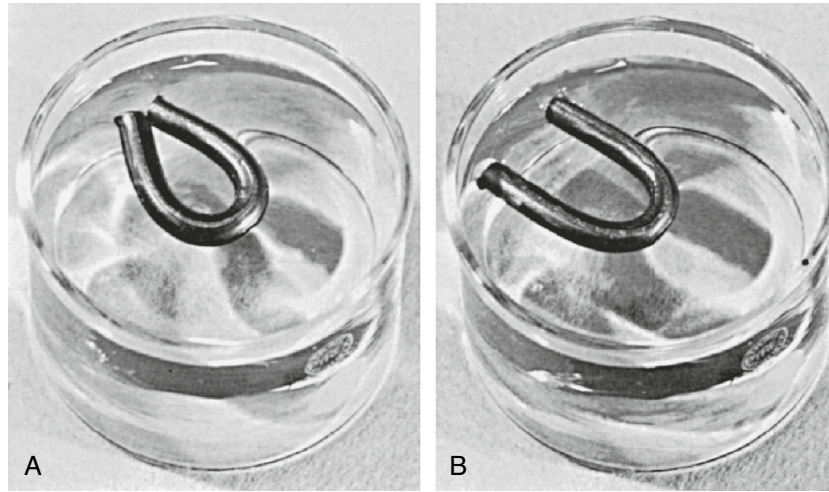
To preserve their properties, dental waxes must be warmed homogeneously but not over a prolonged time. Dry heat is preferred to the use of a water bath to avoid incorporating water. To fabricate indirect patterns on a die, the die should be lubricated. The melted wax may be added in layers with a spatula or a waxing instrument. When the margins are being carved, care should be taken to avoid abrading any

surface of the stone die. A silk or other fine cloth may be used for a final polishing of the pattern, rubbing toward the margins.

Waxes are thermoplastic polymers that tend to return partially toward their original shape after manipulation over time. This is known as **elastic memory**, as illustrated in Figure 13-28. When wax is bent into a horseshoe, the molecules in the inner bend are under compression, and those in the outer bend are in tension. Once the stresses are gradually relieved at room temperature, the wax tends to recover its elastic strain. However, some clinicians prefer to apply finger pressure as the wax is cooling to help fill

the cavity and prevent distortion during cooling. The fingers also accelerate the cooling rate. Although temperature changes should be avoided, some technicians prefer to repeatedly remelt small areas along the margins and examine them under a low-power microscope.

Regardless of the method chosen, the most practical method for avoiding any possible delayed distortion is to invest the pattern immediately after removal from the mouth or die, as noted earlier. Once the investment hardens (sets), the mission of the wax pattern is accomplished.



• **Figure 13-28** A, A stick of inlay wax is bent into the shape of a horseshoe and floated on water at room temperature. B, After 24 hours, the same stick of wax relaxes and becomes distorted.

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Maintenance of temperature and humidity play key role during storage and transport to prevent distortion. But the study suggests immediate pouring which will minimize the distortion.

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Waxes were shown to be pseudoplastic and did not display a yield point. The pseudoplasticity followed a power law whose exponent was temperature dependent in a complex manner. A standardized viscosity number was defined to characterize the flow behavior of dental waxes. The reciprocal of the pseudoplasticity parameter provides a similarly convenient measure of the stress-sensitivity of the wax.

Yap AU, Yap SH, Teo JC, et al: Microwave drying of high strength dental stone: Effects on dimensional accuracy, *Oper Dent* 28:193–199, 2003.

This study shows that there was no significant difference in percentage weight loss from specimens that were either air dried for 24 h or microwaved at each time interval. Significant differences in dimensional change were observed between specimens microwaved at higher energy levels with shorter duration, and those air dried for 24 h.

Full Selected Readings for this chapter can be found on www.expertconsult.com.

Suggested Readings (Web Version)

Impression Materials

Abdelraouf RM: Chemical analysis and microstructure examination of extended-pour alginate impression versus conventional one (characterization of dental extended-pour alginate), *Int J Polym Mater* 67:612–618, 2018.

The extended-pour dental alginate showed higher calcium/sodium ratio, lower organic content, and higher powder:water ratio than the conventional one, which may contribute to increasing its dimensional stability. On the other hand, the functional groups and the microstructure did not show variation between both alginate types.

Balkenhol MS, Haunschild S, Lochnit G, et al: Surfactant release from hydrophilized vinylpolysiloxanes, *J Dent Res* 88:668–672, 2009.

Water droplets placed on the hydrophilized VPS absorbed surfactant from the VPS reduced the surface tension of the water droplet. It resulted in lower contact angle over time; surface properties of the VPS did not change.

Barnes HA: Thixotropy—a review, *J Non-Newton Fluid* 70:1–33, 1997.

This review article describes in detail the thixotropic phenomenon with examples of thixotropic systems.

Batchelor JM, Todd PM: Allergic contact stomatitis caused by a polyether dental impression material, *Contact Derm* 63:296–297, 2010.

Bertolo MVL, de Oliveira Tomaselli L, Vitti RP, et al: Accuracy of partially edentulous arch impressions obtained from different alginates and storage times, *Braz J Oral Sci* 15:252–257, 2016.

The study concluded that the alginate impressions investigated could be stored for up to 5 days.

Blatz MB, Sadan A, Burgess JO, et al: Selected characteristics of a new polyvinyl siloxane impression material: A randomized clinical trial, *Quintessence Int* 36:97–104, 2005.

Hydrophilized PVS impression material provided a significantly higher proportion of impressions free of bubbles and voids than the non-hydrophilized PVS.

Boening KW, Walter MH, Schuette U: Clinical significance of surface activation of silicone impression materials, *J Dent* 26:447–452, 1998.

This study shows no significant correlation between sulcus reproduction and free surface energy or between quality ranking and free surface energy.

Bradna P, Cerna D: Impact of water quality on setting of irreversible hydrocolloid impression materials, *J Prosthet Dent* 96:443–448, 2006.

The use of tap water with high water hardness accelerated setting of alginate impression as opposed to the use of distilled water.

Chai J, Pang I-C: A study of the “thixotropic” property of elastomeric impression materials, *Int J Prosthodont* 7:155–158, 1994.

The study shows shear thinning does not have a lasting effect on the viscosity of vinyl polysiloxane, polyether, or polysulfide.

Chen SY, Liang WM, Chen FN: Factors affecting the accuracy of elastomeric impression materials, *J Dent* 32:603–609, 2004.

This study evaluates the effects of storage times and the proportion of inorganic filler on the accuracy and stability of elastomeric impression materials.

Craig RG: Review of dental impression materials, *Adv Dent Res* 2:51–64, 1988.

This article reviews published works from 1975 to 1986. Advances during the period included disinfection solutions, the agar/alginate technique, dustless alginate, new formulations of polyether and PVS, elimination of hydrogen gas from PVS, the static mixing of PVS, and hydrophilization of PVS.

Davis BA, Powers JM: Effect of immersion disinfection on properties of impression materials, *J Prosthodont* 3:31–34, 1994.

Two 30-min cycles of disinfection in 2% acid-potentiated glutaraldehyde reduced wettability but had little effect on the dimensional change of addition silicones and polyethers.

Grundke K, Michel S, Knispel G, et al: Wettability of silicone and polyether impression materials: Characterization by surface tension and

contact angle measurements, *Colloids Surf A: Physicochem* 317:598–609, 2008.

The decrease of the water contact angle was directly related to the decrease in the liquid surface tension of the water droplet during spreading. The migration of the surfactant to the outermost surface was increasingly hindered with the progression of the polymerization and cross-linking process.

Hosseinpour D, Berg JC: The dynamic interaction of water with four dental impression materials during cure, *J Prosthodont* 18:292–300, 2009. All materials investigated in the fresh, uncured state showed qualitative decomposition, such as formation of a crater and a scum of material at its surface, from interaction with probing water. These effects diminished with curing time until, beyond a critical value, no effects were evident. The initial hydrophilicity was highest for polyether. Beyond the critical curing time, different degrees of hydrophilicity were observed, with Aquasil showing the lowest final contact angle.

Kim K-N, Craig RG, Koran A: Viscosity of monophase addition silicones as a function of shear rate, *J Prosthet Dent* 67:794–798, 1992.

All products showed a 6- to 10-fold decrease in viscosity with an increasing shear rate (shear thinning).

Klooster J, Logan GL, Tjan AHL: Effects of strain rate on the behavior of elastomeric impressions, *J Prosthet Dent* 66:292–298, 1991.

This study reported that (1) polysulfide exhibited the greatest deformation with the lowest tensile strengths; (2) higher strain rates yielded higher tensile strength; and (3) polysulfides showed the greatest elongation at rupture, with the highest values for higher strain rates.

Kulkarni MM, Thombare RU: Dimensional changes of alginate dental impression materials—an in vitro study, *J Clin Diagn* 9:98–102, 2015.

Maintenance of temperature and humidity play key role during storage and transport to prevent distortion. But the study suggests immediate pouring which will minimize the distortion.

Lim K-C, Chong Y-H, Soh G: Effect of operator variability on void formation in impressions made with an automixed addition silicone, *Aust Dent J* 37:35–38, 1992.

Automixing produced substantially fewer voids than hand mixing. There was a significant difference in the number of voids in the impressions made by the two operators.

Lu H, Nguyen B, Powers JM: Mechanical properties of 3 hydrophilic addition silicone and polyether elastomeric impression materials, *J Prosthet Dent* 92:151–154, 2004.

The study shows that a new “soft” polyether impression material had higher strain in compression and lower tensile strength compared to new “hydrophilic” addition silicone materials.

Martinez JE, Combe EC, Pesun IJ: Rheological properties of vinyl polysiloxane impression pastes, *Dent Mater* 17:471–476, 2001.

Both PVS materials investigated in the study exhibited thixotropic properties.

Martins F, Branco P, Reis J, et al: Dimensional stability of two impression materials after a 6-month storage period, *Acta Biomater Odontol Scand* 3:84–91, 2017.

One polyether and one PVS were stored at 23 °C for 6 months and exhibited dimensional changes below the maximum permitted by the ISO 4823:2000.

McCabe JF, Carrick TE: Recording surface detail on moist surfaces with elastomeric impression materials, *Eur J Prosthodont Restor Dent* 14:42–46, 2006.

It was concluded that the more hydrophilic nature of the polyether and hybrid materials enabled them to record more accurate impressions of moist surfaces, particularly in areas of difficult access such as deep grooves.

McCormick JT, Antony SJ, Dial ML, et al: Wettability of elastomeric impression materials: Effect of selected surfactants, *Int J Prosthodont* 2:413–420, 1989.

There are two distinct groups of impression materials classified by surface wettability: agar, alginate, and polyether are hydrophilic, while polysulfide and silicone (not hydrophilized) are more hydrophobic.

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- Norling BK, Reisbick MH: The effect of nonionic surfactants on bubble entrapment in elastomeric impression materials, *J Prosthet Dent* 42:342–347, 1979. The incorporation of nonionic surfactants into silicone and polysulfide elastomers increases their wettability by gypsum products and results in fewer bubbles in poured casts.
- Pandey P, Mantri S, Bhasin A, et al: Mechanical properties of a new vinyl polyether silicone in comparison to vinyl polysiloxane and polyether elastomeric impression materials, *Contemp Clin Dent* 10:203–207, 2019. A combination of vinyl polysiloxane (VPS) and polyether (PE) elastomers called “polyvinyl ether silicone” is shown to be more flexible with high tensile energy.
- Penfold RdRS, Brandt WC, Miranda ME, et al: Evaluation of dimensional stability and details reproduction of alginate molds storage in different times and temperature, *Braz Dent Sci* 21:37–43, 2018.
- Pratten DH, Novetsky M: Detail reproduction of soft tissue: A comparison of impression materials, *J Prosthet Dent* 65:188–191, 1991. Polyether and hydrophilized addition silicone were judged best in detail reproduction and ZOE and polysulfide low-viscosity materials were judged worst in this regard. Voids were minimized with low-viscosity polysulfide and ZOE relative to addition silicones.
- Re D, De Angelis F, Augusti G, et al: Mechanical properties of elastomeric impression materials: An in vitro comparison, *Int J Dent* 4(4282861-8), 2015. The light-body vinylpolyether silicone showed high tensile strength, yield strength, and adequate strain at yield/break.
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- Salem NS, Combe EC, Watts DC: Mechanical properties of elastomeric impression materials, *J Oral Rehab* 15:125–132, 1988. This study investigated four elastomeric impression materials. The polysulfide had the greatest resistance to tear, but the elastic modulus and tensile strength were less than that of the other three materials.
- Sinjari B, D’Addazio G, Xhajanka E, et al: Penetration of different impression materials into exposed dentinal tubules during the impression procedure, *Materials (Basel)* 13(13211-10), 2020. The study shows that the impression materials can penetrate and remain entrapped inside the dentinal tubules during the impression procedures. This aspect might have a negative influence on the adhesion, and thus this study strongly supports the use of an immediate dentine sealing procedure for adhesive restorations.
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- Wassell RW, Ibbetson RJ: The accuracy of polyvinyl siloxane impressions made with standard and reinforced stock trays, *J Prosthet Dent* 645:748–757, 1992. Using stock trays, the heavy-body/light-body combination was superior to the putty-wash impression made with the addition silicone.
- Webber RL, Ryge G: The determination of tear energy of extensible materials of dental interest, *J Biomed Mater Res* 2:281–296, 1968. An equation was used that takes dimensional change of the test specimen into consideration in calculating tear energy.

Gypsum Products

- Adrien J, Meille S, Tadier S, et al: In-situ x-ray tomographic monitoring of gypsum plaster setting, *Cem Concr Res* 82:107–116, 2016.
- Bailey JH, Donovan TE, Preston JD: **The dimensional accuracy of improved dental stone, silver-plated, and epoxy resin die materials**, *J Prosthet Dent* 59:307–310, 1988. Silver-plated and epoxy resin die systems were found to be acceptable alternatives to the improved dental stones.
- Berg E, Nielsen O, Skaug N: High-level microwave disinfection of dental gypsum casts, *Int J Prosthodont* 18:520–525, 2005. Microwave treatment was capable of eliminating microorganisms on gypsum casts, whereas casts poured from disinfected alginate impressions were not free of microorganisms.
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- Chan TKC, Darvell BW: Effect of storage conditions on calcium sulphate hemihydrate-containing products, *Dent Mater* 17:134–141, 2001. This article shows that at a relative humidity less than 70%, it would take in excess of 1000 h of exposure before reaction within the gypsum products began. There is no evidence to suggest that there is a safe humidity level for exposure.
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The article describes the reaction occurring in three steps: Dissolution, nucleation, and precipitation, as well as completion associated with depletion of reactants.

Lucas MG, Arioli-Filho JN, Nogueira SS, et al: Effect of incorporation of disinfectant solutions on setting time, linear dimensional stability, and detail reproduction in dental stone casts, *J Prosthodont* 18:521–526, 2009.

This article shows that addition of sodium hypochlorite significantly alters, adversely, all of the evaluated properties. However, the addition of glutaraldehyde and chlorhexidine induces no significant changes in the evaluated properties.

Mahler DB, Ady AB: Explanation for the hygroscopic setting expansion of dental gypsum products, *J Dent Res* 39:578–589, 1960.

This is a classic study that best defines the mechanics of hygroscopic expansion.

Proença JDS, Suzuki MM, da Costa SC, et al: Influence of different water types on the physical and mechanical properties of gypsum, *Braz J Oral Sci* 14:199–203, 2015.

The type of water, slurry, mineral, or distilled water study exhibits no statistical difference in physical and mechanical properties.

Vyas R, Vaddamanu SK, Gurumurthy V, et al: Variations in the compressive strength of a die stone with three different sulfates at eight different concentrations: An in vitro study, *J Contemp Dent Pract* 20:1297–1306, 2019.

Chemical additives such as sulfate salts may increase the CS such that the die stone can withstand clinical and laboratory handling forces.

Yap AU, Yap SH, Teo JC, et al: Microwave drying of high strength dental stone: Effects on dimensional accuracy, *Oper Dent* 28:193–199, 2003.

This study shows that there was no significant difference in percentage weight loss from specimens that were either air dried for 24 h or microwaved at each time interval. Significant differences in dimensional change were observed between specimens microwaved at higher energy levels with shorter duration, and those air dried for 24 h.

Dental Wax

Baum L, Phillips RW, Lund MR: *Textbook of Operative Dentistry*, ed, 3, Philadelphia, 1995, Saunders.

Techniques for manipulating wax and forming the pattern are described.

Craig RG, Eick JD, Peyton FA: Strength properties of waxes at various temperatures and their practical application, *J Dent Res* 46:300–305, 1967.

Properties of waxes are controlled by the composition and melting range of certain components.

Kotsiomiti E, McCabe JF: Stability of dental waxes following repeated heatings, *J Oral Rehabil* 22:135–143, 1995.

The flow and strength properties of dental waxes were examined following excessive and repeated heating. Repeated exposure of dental waxes to temperatures higher than 200 °C may affect the composition and properties, resulting in inferior materials.

McMillan LC, Darvell BW: Rheology of dental waxes, *Dent Mater* 16:337–350, 2000.

Waxes were shown to be pseudoplastic and did not display a yield point. The pseudoplasticity followed a power law whose exponent was temperature dependent in a complex manner. A standardized viscosity number was defined to characterize the flow behavior of dental waxes. The reciprocal of the pseudoplasticity parameter provides a similarly convenient measure of the stress-sensitivity of the wax.

Michalakakis KX, Kapsampeli V, Kitsou A, et al: Marginal adaptation of four inlay casting waxes on stone, titanium, and zirconia dies, *J Prosthet Dent* 112:70–78, 2014.

A significant correlation was found between the marginal accuracy and the contact angle values. As the contact angle value became smaller, the marginal accuracy improved.

Taha D, Nour M, Zohdy M, et al: The effect of different wax pattern fabrication techniques on the marginal fit of customized lithium disilicate implant abutments, *J Prosthodont* 28:1018–1023, 2019.

Wax patterns for pressing lithium disilicate abutments were made by CAD/CAM milling, 3D printing, and conventional layering. The conventional layering pattern and resultant pressed prostheses exhibits the best fit to the titanium insert among the three methods of fabricating wax patterns.

14

Casting Investments and Casting Procedures

OUTLINE

Preparation of the Master Die

Wax Pattern and Sprue Design

Investment Materials

Investing Procedure

Casting Procedure

Clinical Evaluation of Casting Fit

Causes of Defective Castings

KEY TERMS

Burnout Process of heating an invested mold to eliminate the embedded wax or plastic pattern.

Casting (1) The process by which a wax pattern is converted to a metallic replica of a prepared tooth restoration. (2) A dental restoration formed by the solidification of a molten metal in a mold.

Hygroscopic expansion Amount of setting expansion that occurs when a gypsum-bonded casting investment is immersed in

38 °C water during setting. (See [Chapter 13](#), Auxiliary Materials, for more information on this process.)

Refractory Capable of sustaining exposure to a high temperature without significant degradation.

Sprue The mold channel through which molten metal or ceramic flows into a mold cavity.

Sprued wax pattern A wax form consisting of the prosthesis pattern and the attached ingate or sprue network.

The lost wax method has been used to fabricate prostheses made of metal, ceramic, and polymers. Although the principle of the process is the same for all three classes of materials, there are distinct differences unique to each material. Fabrication of ceramic- and polymer-based prostheses was presented in [Chapters 10 \(Fabrication of Metal-Ceramic Prostheses\)](#) and [11 \(Heat-Activated Denture Base Resins\)](#), respectively. This chapter will focus on the metals only.

The process requires a die that duplicates the oral tissue needing a replacement or prosthesis. A wax pattern ([Figure 14-1](#)) of the prosthesis is built on the laboratory indirect die by carving wax to the exact dimension. The wax pattern is then removed from the die and placed in a casting ring to be filled with investment materials. After the investment sets, the casting ring is heated to melt and burn out the wax. The investment material in the casting ring is now a negative of the final prosthesis. The negative mold is then filled with molten metal. After the metal cools, the investment is fragmented and removed, leaving the prosthesis. This is a very brief description of the process. In practice, there are many fine details. The focus of this chapter is first to prepare a die suitable for fabricating the wax pattern. The wax pattern is then fixed in a casting ring with cylindric segments known as an *ingate* or *sprue* for the flow of molten metal to fill the mold cavity, made by investing in a **refractory** material ([Figure 14-2](#)). The molten metal

is introduced to the empty space with pressure. Finally, there is a discussion of casting defects.

CRITICAL QUESTION

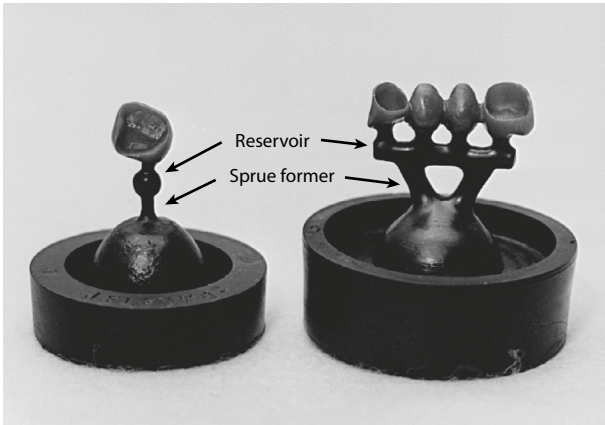
What methods can be used to increase the abrasion resistance of master dies?

Preparation of the Master Die

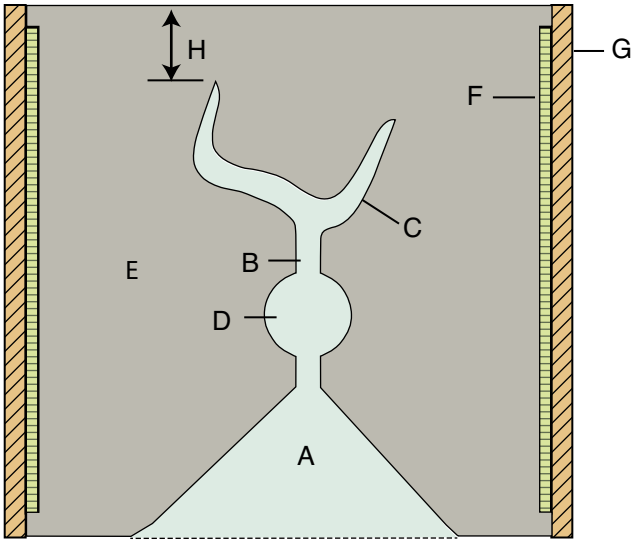
The most commonly used die materials are type IV and type V improved gypsum dental stones ([Chapter 13, Types of Gypsum Products](#)). Type IV stones have a setting expansion of 0.1% or less, whereas type V stones may expand as much as 0.3%. This greater expansion is useful in compensating for the relatively large solidification shrinkage of base-metal alloys.

The chief disadvantage of the type IV gypsum die is its susceptibility to abrasion during carving of the wax pattern. To overcome deficiencies of gypsum dies, several modifications or different materials have been used:

- Silver or copper plating, coating the surface with cyanoacrylate adhesive, or adding a die hardener to the gypsum can be used to improve abrasion resistance of gypsum master dies.
- Several coats of resin-based spacer, such as nail polish, can be painted on a stone die away from the margins of the restoration



• **Figure 14-1** Primary sprue oriented directly toward the wax pattern (left). Note the spherical reservoir on the vertical sprue. Indirect sprue design showing a horizontal reservoir runner bar that is positioned near the heat center of the invested ring (right).



• **Figure 14-2** Diagrammatic representation of a dental casting mold: A, Crucible former. B, Sprue. C, Cavity formed by wax pattern after burn-out. D, Reservoir. E, Investment. F, Liner. G, Casting ring. H, Recommended maximum investment thickness of approximately 6 mm between the end of the mold cavity and the end of the invested ring to provide pathways for sufficient gas escape during casting.

- to produce relief space for cement luting agent and ensure complete seating of an otherwise precisely fitting **casting** or coping.
- To eliminate the possibility of distortion of the wax pattern on removal from the die or during the setting of the investment, one technique is to pour up the die with an investment material with comparable properties to die materials.
 - Nongypsum die materials, such as acrylic, polyester, and epoxy resins, are used because of their superior abrasion resistance. Compatibility between die material and the impression material is specific to the brand rather than to chemical types of impression materials. Even though these dies are generally undersized in comparison with the prepared tooth, they are used successfully, presumably because dimensional compensation has occurred during the investing and casting procedure.

TABLE 14-1 Dimensional Change in Dies Made From a Silicone Impression Compared With a Standardized Die

Die material	DIMENSIONAL CHANGE (%)	
	Occlusal	Cervical
Type IV die stone	0.06	0.00
Type IV stone plus hardener A	0.16	0.08
Type IV stone plus hardener B	0.10	0.10
Silica-filled epoxy resin	−0.15	−0.26
Aluminum-filled epoxy resin	−0.14	−0.19
Electroformed silver	−0.10	−0.20

Reproduced with permission from Toreskog S, Phillips RW, Schnell RJ: Properties of die materials: a comparative study, *J Prosthet Dent* 16:119, 1966.

- Several gypsum die stones have been compounded with resins to provide the advantages of both materials. These modified die stones maintain the low expansion of conventional die stone, but they also have the increased toughness and resistance to carving imparted by the resins.
- Metal dies produced from electroplated impression material have moderately high strength, adequate hardness, and excellent abrasion resistance. The first step is treating the impression to make it conductive to electrical current. The metallized impression is the cathode in the electroplating bath, along with a silver plate as the anode. A direct current is applied to transfer silver from the plate to the impression, a reverse process of corrosion discussed in [Chapter 3, Electrochemical Properties](#). The impression is then filled with dental gypsum stone. When the stone sets, a die with an electroformed metal shell is obtained.

It is important to note that some of the methods described can alter the die dimensions slightly, thus reducing accuracy ([Table 14.1](#)).

CRITICAL QUESTION

What casting deficiencies may result when: (1) the sprue former is too small in diameter, (2) the sprue former is attached without flaring to thinner areas, (3) the sprues are oriented toward thin areas of a wax pattern, or (4) the sprues are of inadequate length to position the wax pattern less than 6 mm from the end of the invested ring?

Wax Pattern and Sprue Design

To provide a pathway or ingate to the mold cavity for molten metal, the wax or resin pattern must have one or more cylindrical wax segments attached at the desired point(s) of metal entry; this arrangement is termed a **sprued wax pattern**. A **sprue** is the channel in a refractory investment mold through which molten metal flows. After the wax pattern has been made, a sprue-former base is attached to the sprued wax pattern, an investment ring is pressed into the sprue-former base, and an investment slurry is vibrated into the ring to embed the wax pattern in the investment, usually under vacuum. Examples of sprued wax patterns on a sprue-former base are shown in [Figure 14-1](#).

The diameter, the length of the sprue former (also referred to simply as the *sprue*), and the position of attachment depend on the

type and size of the pattern, the type of casting machine to be used, and the dimensions of the ring in which the casting will be made.

Wax-Pattern Removal

The sprue former should be attached to the wax pattern with the pattern on the master die, provided that the pattern can be removed directly in line with its path of withdrawal from the die. Any motion that might distort the wax pattern should be avoided during removal. The gauge selection and design for the sprue former are often empirical, but optimal performance during the casting process is based on the five general principles discussed in the following subsections.

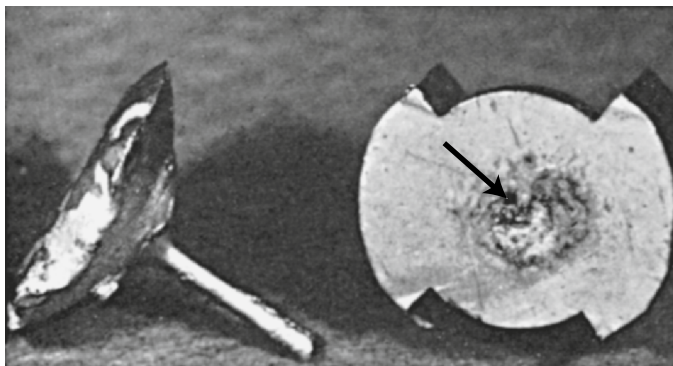
Sprue Diameter

Select a sprue former with a diameter that is approximately the same size as the thickest bulk of the wax pattern. If the pattern is small, the sprue former must also be small because attaching a large sprue former to a thin, delicate pattern could cause distortion. On the other hand, if the sprue former's diameter is too small, it may solidify before the casting itself, and localized shrinkage porosity ("suck-back" porosity) may develop. As shown in Figure 14-3, reservoir sprues are used to help overcome this problem.

Sprue Position and Attachment

The sprue-former connection to the wax pattern is generally flared for higher-density gold alloys but often restricted for lower-density alloys. Flaring of the sprue former may act in much the same way as a reservoir, smoothing the entry of the fluid alloy into the pattern area with less turbulence. The position of the sprue-former attachment is often a matter of individual judgment and intuition, based on the shape and form of the wax pattern. As indicated earlier, the ideal area for the sprue former is the point of greatest bulk in the pattern to avoid distorting thin areas of wax during attachment to the pattern and permit complete flow of the alloy into the mold cavity.

Then, it is best for the molten alloy to flow from a thick section to surrounding thin areas (e.g., the margins). The sprue former should not be attached to a broad, flat surface at a right angle. Such an orientation leads to turbulence within the mold cavity and porosity in this region (Figure 14-4, *A*). When this same pattern is sprued at a 45-degree angle to the proximal area, a satisfactory casting is obtained (Figure 14-4, *B*).



• **Figure 14-3** Localized shrinkage (*pointer*) caused by using a sprue diameter thinner than required.

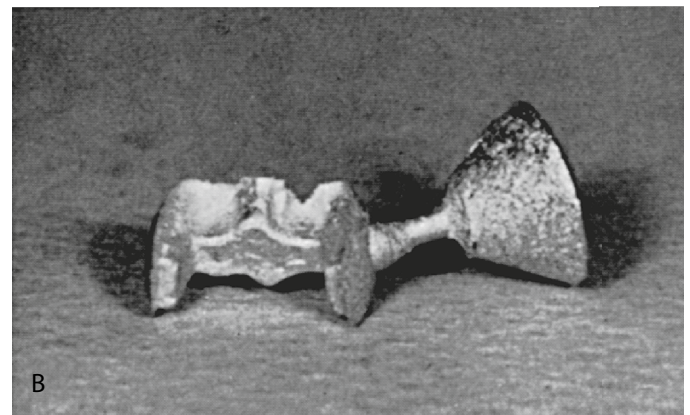
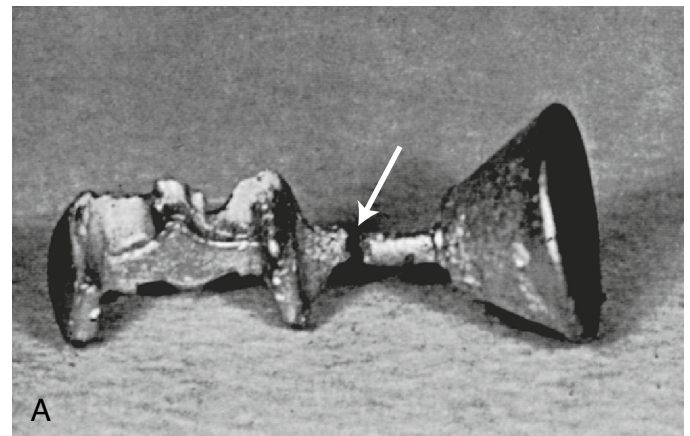
The sprue former should be long enough to position the pattern properly in the casting ring within 6 mm of the trailing end (Figure 14-2) and yet short enough so that the molten alloy does not solidify before it fills the mold.

A reservoir should be added to a sprue network to prevent localized shrinkage porosity (Figure 14-3). When the molten alloy fills the heated casting ring, the pattern area should solidify first, and the reservoir last. The molten metal in the reservoir remains molten to furnish additional liquid alloy into the mold as it solidifies.

The length of the sprue former depends on the length of the casting ring. If the sprue is too short, the wax pattern may be so far removed from the end of the casting ring that gases cannot be adequately vented to permit the molten alloy to fill the ring completely. When these gases are not eliminated, the casting will be incomplete. The sprue length should be adjusted so that the top of the wax pattern is within 6 mm of the open end of the ring for gypsum-bonded investments (Figure 14-2) and within 3 to 4 mm of the top of the phosphate-based investment.

Investment Materials

The material for making the mold must be refractory and thermally stable so that it can withstand exposure to the high temperatures of molten metal as the metal solidifies and cools to room



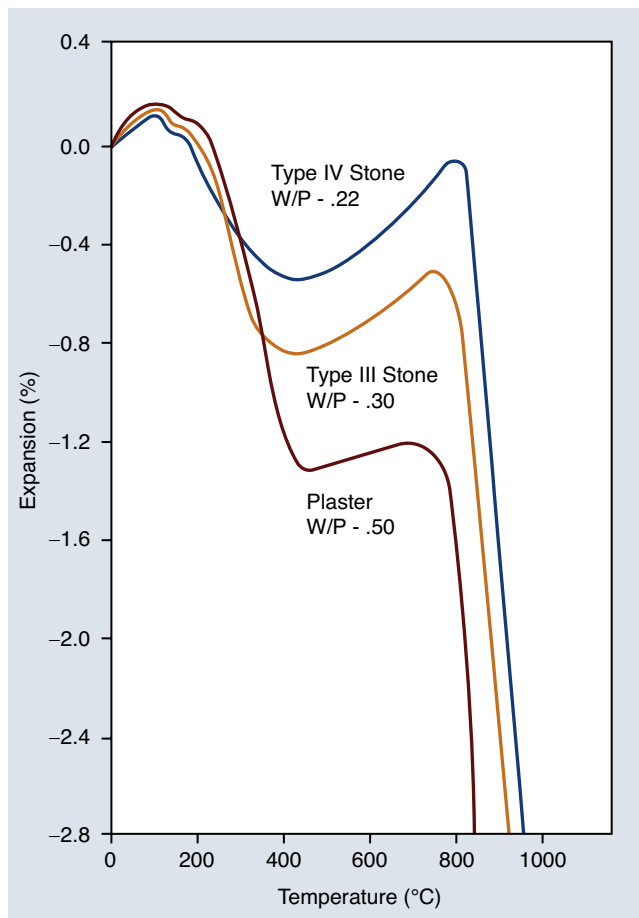
• **Figure 14-4** Effect of sprue orientation. **A**, Detached sprue indicates severe porosity at the point of attachment because of turbulence caused by an improper sprue angle. **B**, Sound casting results with the sprue at approximately 45 degrees to the proximal wall.

temperature. In addition, the mold or investment material must not interact chemically with the metal surface, and it must be easy to remove from the metal casting.

Generally, two types of investments—gypsum-bonded and phosphate-bonded—are employed, depending on the melting range of the alloy to be cast. A third type is the ethyl silicate-bonded investment, which is used principally for the casting of removable partial dentures made from base metals (cobalt-based and nickel-based alloys). Because the thermal contraction coefficients of the alloys are higher than that of the investment mold, the dimension of the prosthesis when cooled to room temperature will be smaller in dimension than the wax pattern's intended dimension. The difference of the dimension is called *casting shrinkage*. To obtain a prosthesis of the intended dimension, the investment mold needs to expand during setting and expand more during **burnout** to compensate for the casting shrinkage.

Gypsum-Bonded Investments

The gypsum-based materials represent the type traditionally used for casting gold alloys. There are two classifications by International Organization for Standardization (ISO) 7490 (American National Standards Institute [ANSI]/American Dental Association [ADA] 126): type 1 is used for casting inlays, onlays, crowns, or other fixed prostheses, and type 2 is used for removable partial denture frameworks.



• **Figure 14-5** Dimensional change of three forms of gypsum when heated. (Courtesy R. Neiman, Whip Mix Corporation, Louisville, KY.)

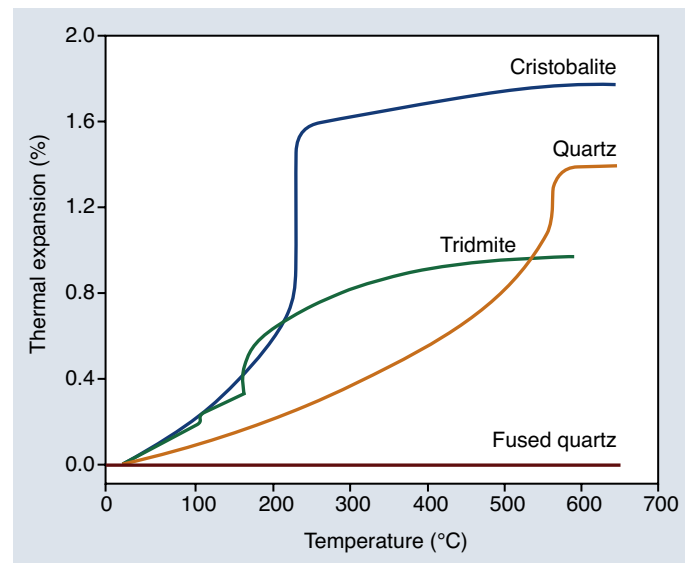
Composition

The ingredients of gypsum-based investments are α -hemihydrate of gypsum as binder, polymorphs of silica as fillers, and other ingredients as modifiers.

The binder holds the filler together and provides the investment strength. When the binder is heated at temperatures sufficiently high to completely dehydrate the investment, it shrinks considerably, and occasionally fractures. As [Figure 14-5](#) shows, when the temperature is raised to 200 to 400 °C, it dehydrates and shrinks. A slight expansion occurs between 400 and 700 °C, and a large contraction then takes place at higher temperatures, caused by decomposition of the calcium sulfate. Thus it is imperative that gypsum investments not be heated above 700 °C.

To compensate for the inherent contraction associated with gypsum and casting shrinkage, polymorphs of silica are incorporated in the investment. Silica exists in at least four polymorphs: quartz, tridymite, cristobalite, and fused quartz. When quartz, tridymite, or cristobalite is heated, a change in crystalline form occurs at transition temperatures characteristic of each polymorph of silica ([Figure 14-6](#)). This crystalline transition is called an *inversion*. Each crystalline transition from lower temperature (α phase) to higher temperature (β phase) is accompanied by a linear expansion. For example, the inversion completes at 573 °C for quartz, at 200 and 270 °C for cristobalite, and at 117 and 163 °C for tridymite. In powdered form, the inversions occur over a temperature range rather than instantaneously at a specific temperature. By the quantity of thermal expansion shown in [Figure 14-6](#), quartz and cristobalite are of particular dental interest.

In addition to silica, certain modifying agents, coloring matter, and reducing agents, such as carbon and powdered copper, are present. The reducing agents are used to provide a nonoxidizing atmosphere in the mold when a gold alloy is cast. Some of the modifiers not only regulate the setting expansion and the setting time but also prevent most of the shrinkage of gypsum when it is heated above 300 °C. In some instances, the modifiers are needed to regulate the setting time and setting expansion, as described for the dental stones.



• **Figure 14-6** Thermal expansion of four polymorphs of silica. (Courtesy R. Neiman, Whip Mix Corporation, Louisville, KY.)

Setting Expansion

Typically, the setting expansion of these investments is controlled by retarders and accelerators for the gypsum. The exothermic heat of gypsum setting can result in expansion of the wax pattern before the investment sets, influencing the effective setting expansion. The expansion of the investment may cause distortion of the wax pattern. Consider a mesio-occluso-distal (MOD) restoration as an example; the investment inside of MOD can force the proximal walls of the wax pattern outward as it sets. If the pattern has a thin wall, the effective setting expansion is somewhat greater than that for a pattern with thicker walls because the investment can move the thinner wall more readily. Also, the softer the wax, the greater the effective setting expansion because the softer wax is more readily deformed by the expanding investment. If a softer wax is used, the setting expansion may cause excessive distortion of the pattern.

Hygroscopic Setting Expansion

As illustrated in Figure 14-7, the hygroscopic setting expansion may be six or more times greater than the normal setting expansion of a dental investment. If greater expansion is needed, there are many factors in the control of **hygroscopic expansion**.

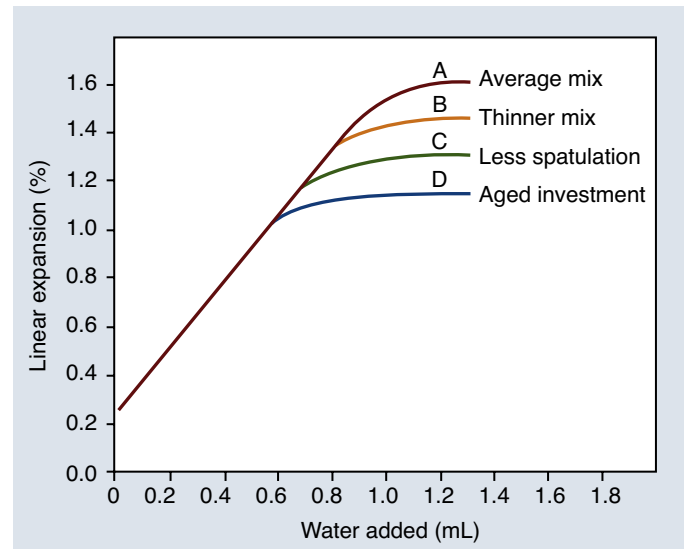
The magnitude of hygroscopic setting expansion is generally proportional to the silica content of the investment, which becomes greater with a finer size of silica. Filler plays no role in hygroscopic expansion; it is the interface between filler and gypsum that allows added water to diffuse through the setting material and increased expansion.

As discussed for gypsum products, the higher the water/powder (W/P) ratio of the original investment water mixture, the less the hygroscopic setting expansion. As the mixing time is reduced, the hygroscopic expansion is decreased. The older the investment, the lower is its hygroscopic expansion. The greatest amount of hygroscopic setting expansion is observed if the immersion takes place before the initial set. The longer the immersion of the investment in the water bath is delayed beyond the time of the initial

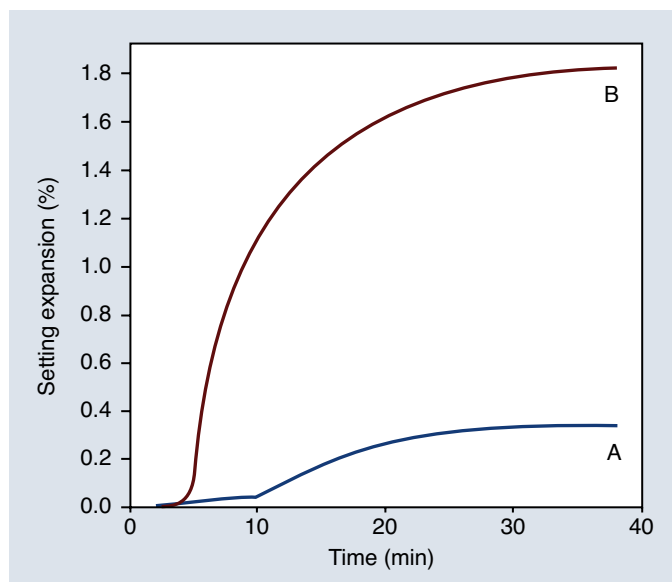
set of the investment, the lower the hygroscopic expansion. The effects of the W/P ratio, mixing, and shelf life on the maximal hygroscopic setting expansion are illustrated in Figure 14-8 relative to the amount of water added during setting.

Thermal Expansion

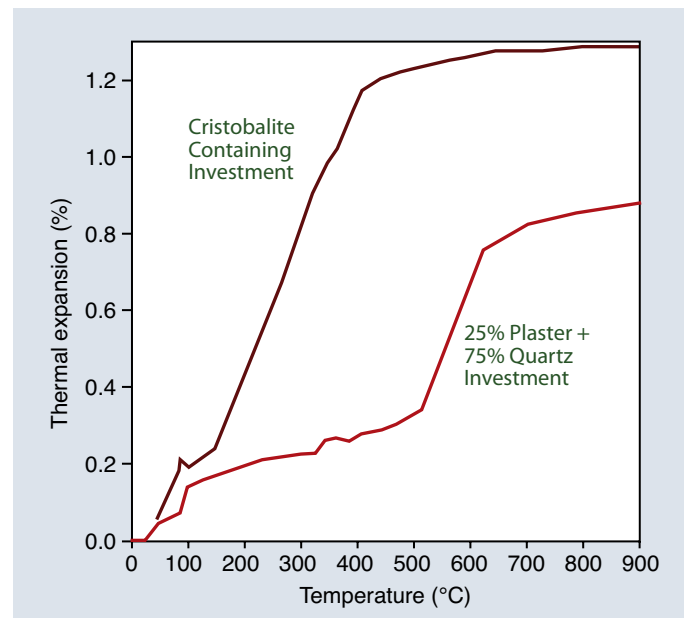
The effect of cristobalite compared with that of quartz is demonstrated in Figure 14-9. Because of the much greater expansion that occurs during the inversion of cristobalite, the normal contraction of gypsum during heating is readily eliminated. Furthermore, the expansion occurs at a lower temperature because of the lower



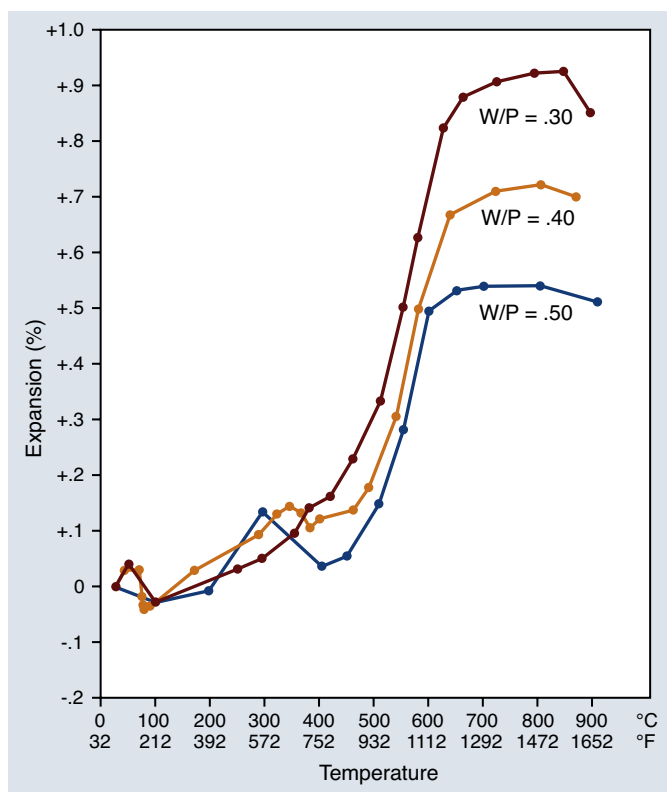
• **Figure 14-8** Relationship of linear hygroscopic setting expansion and amount of water added as influenced by certain manipulative factors. (Data from Asgar K, Mahler DB, Peyton FA: Hygroscopic technique for inlay casting using controlled water additions, *J Prosthet Dent* 5:711-724, 1955.)



• **Figure 14-7** Setting expansion and hygroscopic expansion of a gypsum-bonded investment. **A**, Normal setting expansion of dental investment. **B**, Hygroscopic setting expansion. The investment was immersed in water 5 minutes after the beginning of mixing; the water/powder ratio was 0.30.



• **Figure 14-9** Thermal expansion of an investment that contains 25% plaster of Paris and 75% quartz (*red*) and an investment that contains cristobalite rather than quartz (*brown*). (Courtesy Dr. George Paffenbarger.)



• **Figure 14-10** Effect of water/powder ratio on the thermal expansion of an investment containing 20% plaster of Paris and 80% quartz. (Courtesy Dr. George Paffenbarger.)

inversion temperature of the cristobalite in comparison with that of quartz. A reasonably good fit of the casting is obtained when a gold alloy is cast into the mold at temperatures of 500 °C and higher. The thermal expansion curves of an investment provide some idea of the polymorph of the silica that is present. As can be seen from Figure 14-9, the investments containing cristobalite expand earlier and to a greater extent than those containing quartz. Most current investments are likely to contain both quartz and cristobalite.

The magnitude of thermal expansion is related to the amount of solids present. This effect is demonstrated by the curves shown in Figure 14-10. The same figure also shows that it is imperative to measure the water and powder accurately for proper compensation.

The addition of small amounts of sodium, potassium, or lithium chlorides to the investment eliminates the contraction caused by gypsum and increases the expansion without the need for an excessive amount of silica.

Strength

The strength of an investment is usually measured under compressive stress and is increased according to the amount and type of gypsum binder present. The use of chemical modifiers increases the strength because more of the binder can be used without a marked reduction in thermal expansion. The strength of the investment is affected by the W/P ratio in the same manner as any other gypsum product; the more water employed during mixing, the lower the compressive strength. After the investment has cooled to room temperature, its strength decreases considerably, presumably because of fine cracks that form during cooling.

Although a certain minimal strength is necessary to prevent fracture of the investment mold during casting, the compressive

strength should not be unduly high. When the alloy is still hot and weak, the investment can resist alloy shrinkage by virtue of its strength and constant dimensions. This can cause distortion and even fracture of the casting if the hot strength of the alloy is low.

Porosity of Set Investment

As the molten metal enters the mold under pressure during casting, the trapped air must be forced out ahead of the inflowing metal. If the air is not completely expelled, a back pressure builds up to prevent the molten alloy from completely filling the mold. The simplest method for venting the mold is through the pores of the investment. Thus it is important that the end of a wax pattern that is nearest to the end of the investment ring not be covered by more than 6 mm of investment to allow sufficient interconnectivity of the porous network for the escape of gas from the mold cavity during filling of the mold with molten metal.

Storage

Gypsum-based investments should be stored in airtight and moisture-proof containers. During use, the containers should be opened for as short a time as possible. All investments are composed of several ingredients, each of which possesses a different density. There is a tendency for the components of the investment to separate as they settle, according to their specific gravity. It is advisable to purchase prepackaged investments in relatively small quantities if investments are needed on an infrequent basis.

The investment supplied in bulk packages should be weighed, and the water should be measured according to the proportion of the investment mix. In this manner, one can control the setting or the thermal expansion in relation to the compensation needed for the casting shrinkage and other important properties. One need only measure the gauging water.

One should be aware of slight variations in the weight of premeasured packets of powder. The quality control of investment products is related not only to the homogeneity of particulate components but also to variations in the weight of powder in the packets.

Phosphate-Bonded Investment

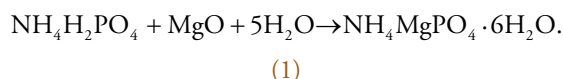
The use of alloys with higher melting temperature ranges, such as those for metal-ceramic restorations, usually leads to greater thermal contraction after solidification. This necessitates an investment material that is more heat resistant with greater expansion. Phosphate-based investments are designed primarily for alloys used to produce copings or frameworks for metal-ceramic prostheses and some base-metal alloys (Chapter 9, Manipulation of Base Metal Alloys).

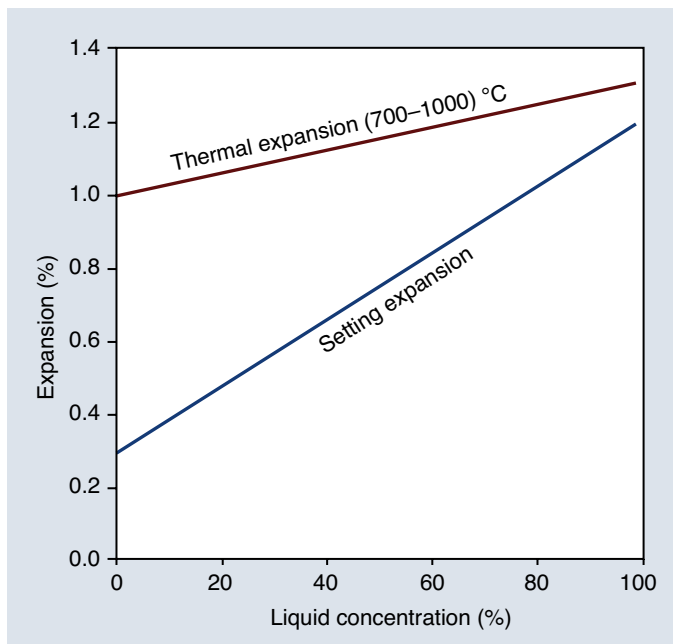
Composition

Phosphate-based investments contain refractory fillers and a binder. The silica filler is typically 80% by weight. The particle size varies from submicron to that of a fine sand. The binder consists of magnesium oxide (basic) and monoammonium phosphate (acidic). A colloidal silica suspension in place of water is used for mixing phosphate investments.

Setting Reaction

The chemical reaction for the phosphate-based binder system is as follows:





• **Figure 14-11** Influence of liquid concentration on the setting and thermal expansion of a phosphate-bonded investment. (Courtesy R. Neiman, Whip Mix Corporation, Louisville, KY.)

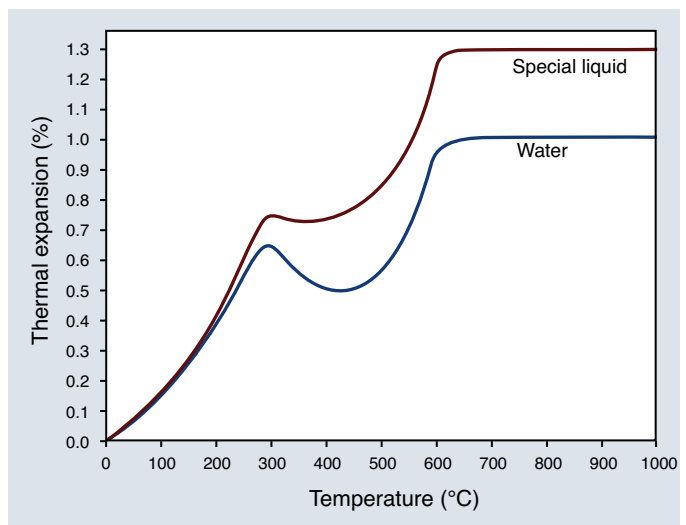
The reaction product is predominantly colloidal multimolecular $(\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O})_n$ aggregate around excess MgO and fillers. On heating, the binder of the set investment undergoes thermal reactions that appear to be the decomposition of $(\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O})_n$. It begins to lose water around 50°C and dehydrates to $(\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O})_n$ at 160°C . Further heating to 300 to 650°C expels the remaining water and ammonia from the phosphate compound and results in a noncrystalline polymeric phase of $(\text{Mg}_2\text{P}_2\text{O}_7)_n$. As the temperature increases, the noncrystalline phase begins to crystallize. The resulting reaction products of phosphate-bonded investments are crystalline $\text{Mg}_2\text{P}_2\text{O}_7$, excess MgO , and essentially unchanged silicas. In addition, $\text{Mg}_3(\text{P}_2\text{O}_4)_2$ may be formed if the investment is grossly overheated above 1040°C or if the molten metal contacts the mold-cavity surfaces.

Setting and Thermal Expansion

The setting reaction yields a slight expansion, which can be increased considerably by using a colloidal silica solution (special liquid) instead of water. Figure 14-11 shows the effect of the concentration of colloidal silica in aqueous suspension on the setting and thermal expansion. Figure 14-12 shows the thermal expansion of a typical phosphate investment mixed with water compared with the same investment mixed with its accompanying special liquid. The early thermal shrinkage of phosphate investments is associated with decomposition of the binder, magnesium ammonium phosphate, and is accompanied by the evolution of ammonia, which is readily apparent by its odor.

Working and Setting Time

The working and setting time of phosphate investments are affected by temperature. The warmer the mix, the faster it sets. Increased mixing time and mixing efficiency result in a faster set and a greater rise in temperature. The ideal technique is to mix as long as possible yet have just enough time for investing.



• **Figure 14-12** Thermal expansion of a phosphate-bonded investment mixed with water compared with the “special liquid.” (Courtesy R. Neiman, Whip Mix Corporation, Louisville, KY.)

Mechanical mixing under vacuum is preferred. The liquid/powder (L/P) ratio also affects the working and setting time; an increase in the L/P ratio increases the working time.

Surface Quality of Cast Metals

The detail reproduction and surface smoothness of a metal-ceramic gold cast in a phosphate-bonded investment are considered inferior to those of a conventional gold alloy cast in a gypsum-bonded investment. Increasing the ratio of “special liquid” to water used for the mix enhances casting surface smoothness but can lead to oversized castings. Improvements in the technique and the composition of phosphate-bonded investments now make it possible to fabricate castings having few surface imperfections on low-fusing gold alloy, high-fusing gold alloy, or base-metal alloy.

Ethyl Silicate-Bonded Investment

The binder of ethyl silicate-bonded investments is a silica gel that reverts to silica (cristobalite) on heating, and the fillers are silicas and magnesium oxide. A colloidal silicic acid is first formed by hydrolyzing ethyl silicate in the presence of hydrochloric acid, ethyl alcohol, and water. The reaction, in its simplest form, can be expressed as follows:



The colloidal sol of silicic acid goes through a condensation polymerization reaction, forming a three-dimensional (3-D) polysilicic network that interacts with silicas, and magnesium oxide is a coherent gel of polysilicic acid forms, accompanied by a setting shrinkage. The addition of magnesium oxide neutralizes acid and strengthens the gel.

This soft gel is dried at a temperature below 168°C . During the drying process, the gel loses alcohol and water to form a concentrated, harder gel. As might be expected, volumetric contraction accompanies drying, which reduces the size of the mold. This contraction is known as *green shrinkage*, which is additive to the setting shrinkage.

The remaining cast is somewhat fragile because the amount of binder is quite low, and it is essentially composed of silica. The wax pattern is formed on a refractory cast and invested in a manner like other investments. However, the process for an ethyl silicate-bonded investment is a little more complicated than that for the phosphate type, in that care must be exercised during handling and burnout because flammable alcohol is given off. If the ethyl silicate-bonded investment is heated to a sufficiently high temperature, some silica converts to quartz and provides added expansion. This type of investment can be heated to between 1090 and 1180 °C and is compatible with the higher-fusing alloys. Its low setting expansion minimizes distortion.

Investing Procedure

The overall procedures involved in investing and casting are quite similar for gypsum-based and phosphate-based investment materials; therefore they are described simultaneously. For best results, the manufacturer's recommendations for the specific alloy used should be followed.

A wax-pattern cleaner should be used to remove any debris, grease, or oils. Excess liquid is shaken off, and the pattern is left to air-dry while the investment is being prepared. The thin film of cleanser left on the pattern reduces the surface tension of the investment mixture, making it "wet" the wax pattern better to ensure complete coverage of the intricate portions of the pattern.

While the wax pattern cleaner is air-drying, the appropriate amount of liquid for the investment material is dispensed in a clean, dry mixing bowl, and the powder is gradually added to the liquid to minimize air entrapment. Hand spatula mixing is performed gently until all the powder has been wet. Although continuing hand-mixing to completion is an option, it is far more common to complete mixing mechanically under vacuum.

Vacuum Mixing

Mechanical mixing under vacuum removes the air bubbles created during mixing and evacuates any potentially harmful gases produced by the chemical reaction of the high-heat investments. Once mixing is complete, the pattern may be hand invested or vacuum invested. For investing by hand, the entire pattern is painted (inside and out) with a thin layer of investment. The casting ring is positioned on the crucible former, and the remainder of the investment is vibrated slowly into the ring. With vacuum investing, the same equipment used to mix the investment is employed to invest the pattern without breaking vacuum.

As noted, the porosity in the investment is reduced by vacuum investing. As a result, the texture of the cast surface is somewhat smoother, with better detail reproduction. The tensile strength of vacuum-mixed investment is also increased. One study found that 95% of vacuum-invested castings were free of nodules, whereas only 17% of castings made in hand-invested molds were entirely free of defects. Freedom of any surface imperfections is highly important because even a small nodule on a casting may damage a fragile enamel margin when the casting is evaluated for fit in the prepared cavity, and thus it may not seat completely. The finished casting should always be checked under magnification for such defects before fitting it on the die.

Air bubbles that remain in the mix, even with vacuum mixing, can be entrapped on flat or concave surfaces that are not oriented suitably for air evacuation. Tilting the ring slightly aids in releasing these bubbles so that they can rise to the surface. Excessive

vibration should be avoided because it can cause solids in the investment to settle and may lead to free-water accumulation adjacent to the wax pattern, resulting in surface roughness. Excessive vibration can also dislodge small patterns from the sprue former, resulting in a miscast.

If the hygroscopic technique is employed, the filled casting ring is immediately placed in a 37 °C water bath with the crucible former's side down. For the thermal expansion or high-heat technique, the invested ring is bench-set undisturbed for the time recommended by the manufacturer.

CRITICAL QUESTIONS

How does nonuniform investment expansion occur? How can excessive longitudinal expansion be minimized?

Control of Shrinkage Compensation

Recall the earlier discussion of controlling casting shrinkages by either setting (includes hygroscopic) expansion or the thermal expansion of the investment. Both techniques are currently in use and are commonly termed the *hygroscopic expansion (low-heat) method* and the *thermal expansion (high-heat) method*. As their names alone might indicate, the high-heat method requires thermal expansion of the investment to occur between room temperature and a high temperature (650 to 700 °C for gypsum-bonded investments, and up to 1030 °C for phosphate-bonded investments). With the low-heat method, the hygroscopic expansion of the investment is responsible for mold enlargement, and the mold is heated between 482 and 510 °C for casting high-noble crown and bridge alloys.

Occasionally, it may be desirable to alter the mold dimensions of a full cast crown compared with a small inlay. Additional steps can be taken to expand the ability to compensate for the inherent casting shrinkage.

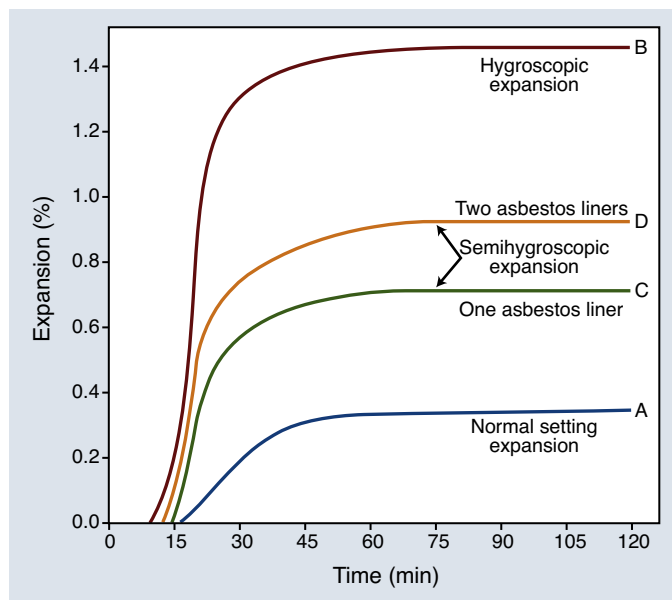
Casting Ring Liner

With the use of solid metal rings or casting flasks, provisions must be made to permit investment expansion in the nonaxial (radial) direction. The mold may become smaller rather than larger because of the reverse pressure resulting from the confinement of the setting expansion. This effect can be overcome by using a split ring or flexible rubber ring that permits the setting expansion of the investment.

However, the most commonly used technique to provide investment expansion is to line the walls of the unsplit casting ring with a liner. Traditionally, asbestos was the material of choice, but it can no longer be used because its carcinogenic potential makes it a biohazard. Two types of nonasbestos ring liner materials have been produced: an aluminosilicate ceramic liner and a cellulose (paper) liner.

To ensure uniform expansion, the clinician or technician cuts the liner to fit the inside diameter of the casting ring with no overlap. The dry liner is tacked in position with sticky wax, and it is then used either dry or wet. With a wet liner technique, the lined ring is immersed in water for a time, and the excess water is shaken away. Squeezing the liner should be avoided because this leads to variable amounts of water removal and nonuniform expansion. Although a ceramic liner may not absorb as much water as a cellulose liner, the ceramic liner's network of fibers can retain water on the surface.

The liner affords greater radial setting expansion in the investment, and the absorbed water causes a semihygroscopic expansion as it is drawn into the investment during setting, as shown for



• **Figure 14-13** Effect of liner and setting condition on the setting expansion. **A**, Normal setting. **B**, Hygroscopic expansion of an investment compared with the somewhat restricted expansion that occurs in an inlay ring containing one liner (**C**) or two liners (**D**). (Courtesy R. Neiman, Whip Mix Corporation, Louisville, KY.)

gypsum investments in Figure 14-13. The use of one liner (C in Figure 14-13) increases the normal setting expansion compared with no liner. Using a thicker liner material or two layers of liner (D in Figure 14-13) provides even greater semihygroscopic expansion and affords a more unrestricted normal setting expansion of the investment. As shown in Figure 14-13, two layers of liner can be used to increase the expansion slightly compared with that obtained from one liner. In any case, the thickness of the liner should not be less than approximately 1 mm.

Because cellulose liners are paper products, they are burned away during the burnout procedure, and a technique must be found to secure the investment in the ring. However, the desired length of the liner remains a matter of controversy. If the length of the liner is somewhat shorter than that of the ring itself, the investment will be confined at one or both ends of the ring. The longitudinal setting and hygroscopic expansion are thereby restricted compared with an arrangement where the liner is flush with the ends of the ring.

The expansion of the investment is always greater in the unrestricted longitudinal direction than in the radial direction—that is, toward the inside of the ring. Therefore it is desirable to reduce the expansion in the longitudinal direction. Placing the liner somewhat short (Figure 14-2) of the ends of the ring tends to produce a more uniform expansion; thus there is less chance for distortion of the wax pattern and the mold.

Altering Liquid/Powder Ratio

As previously discussed, two liners allow for greater setting and thermal expansion than does a single liner (Figure 14-13). Also, the setting, hygroscopic, and thermal expansions of investments can be controlled to a certain extent by varying the L/P ratio of the investment. The lower the L/P ratio, the greater the potential for investment expansion. Conversely, thinner mixes reduce the expansion. With some investments, however, the effect of minor adjustments to the L/P ratio are insignificant.

There is a limit as to how much the L/P ratio can be altered. If the mix is too thick, it cannot be applied to the pattern without a likelihood of distorting the pattern and producing air voids during investing. On the other hand, if the mixture is too thin, a rough surface on the casting may be the result.

Another possible problem is too much expansion of the mold when the thermal expansion technique is used with a cristobalite investment. A thermal expansion of 1.3% may take place. If an effective setting expansion of 0.3% to 0.4% is added to such a thermal expansion, a total linear expansion as high as 1.7% may be obtained, higher than the average thermal casting shrinkage of a gold alloy. As a result, a cast crown may be too large.

In addition to controlling the hygroscopic expansion by the L/P ratio, expansion can be regulated by reducing the time of immersion of the setting investment or by controlling the amount of water to be added during the setting process. The longer the delay before the investment is immersed in the water bath, the less the amount of hygroscopic expansion that can occur.

The modern hygroscopic investment technique generally provides the precise expansion needed for most types of patterns. However, some patterns may require a variation in expansion. Using higher burnout and water-bath temperatures increases the expansion, and vice versa.

Controlled Water-Added Technique

The linear hygroscopic expansion increases directly with the amount of water added until maximum expansion is attained. The compositions of investments used with the water-added hygroscopic casting technique ensure maximal expansion during immersion in water. The amount of hygroscopic expansion needed for compensation is then obtained by adding only enough water to provide the desired expansion.

A soft, flexible rubber ring is used instead of the usual lined metal ring. The pattern is invested as usual. A specified amount of water is then added on top of the investment in the rubber ring, and the investment can set, usually at room temperature. The controlled water-added technique is rarely used, however, because the hygroscopic expansion method described earlier provides adequate expansion in most cases.

Casting Procedure

Once the investment has set for an appropriate period—approximately at least 1 hour for most gypsum- and phosphate-bonded investments—it is ready for burnout. The procedures for the two types of investments are similar, so the following discussion focuses on gypsum investments. The crucible former and any metal sprue formers are carefully removed. Any debris from the ingate area (funneled opening at the end of the ring) is cleaned with a brush. If the burnout procedure does not immediately follow the investing procedure, the invested ring is placed in a humidor at 100% humidity. If possible, the investment should not be permitted to dry out. Rehydration of a set investment that has been stored for an extended period may not replenish all the lost water.

Wax Elimination and Heating

The invested rings are placed in a room-temperature furnace and heated to the prescribed maximum temperature. For gypsum-bonded investments, this temperature can be either 500 °C for the hygroscopic technique or 700 °C for the thermal expansion

technique. With phosphate-bonded investments, the maximum temperature setting may range from 700 to 1030 °C, depending on the type of alloy selected. The temperature setting is more critical for gypsum-bonded investments than for the phosphate type because the gypsum investments are more prone to thermal decomposition. During burnout, some of the melted wax is absorbed by the investment, and residual carbon produced by ignition of the liquid wax becomes trapped in the porous investment. It is also advisable to begin the burnout procedure while the mold is still wet. Water trapped in the pores of the investment reduces the absorption of wax, and as the water vaporizes, it flushes wax from the mold. This process is facilitated by placing the ring with the sprue hole down over a slot in a ceramic tray in the burnout furnace. When the high-heat technique is used, the mold temperature generates enough heat to convert carbon to either carbon monoxide or carbon dioxide. These gases can then escape through the pores in the heated investment.

Hygroscopic Low-Heat Technique

Hygroscopic expansion of gypsum-bonded investment molds was described earlier in this chapter. This technique obtains its compensation expansion from three sources: (1) the 37 °C water bath expands the wax pattern, (2) the warm water entering the investment mold from the top adds some hygroscopic expansion, and (3) the expansion at 500 °C provides the needed thermal expansion. The low-heat technique offers the advantages of less investment degradation, a cooler surface for smoother castings, and the convenience of placing the molds directly into a preheated 500 °C furnace. The last benefit makes it possible to keep one or more furnaces at the burnout temperature so that molds may be put in as they are ready. This is particularly useful in large laboratories where molds are ready for burnout at various times. Care must nevertheless be taken to allow enough burnout time because the wax is more slowly oxidized (eliminated) at the lower temperature.

The molds should remain in the furnace for at least 60 minutes, and they may be held up to 5 hours or longer with little damage. Because the temperature of the furnace is lowered each time a mold is placed, extra time should be allowed to ensure complete wax elimination when molds are placed at intervals. Even though the mold is usually held at this temperature for 60 to 90 minutes, enough residual fine carbon may be retained to reduce the venting of the mold. Because of this potential for reduced venting, back-pressure porosity is a greater hazard in the low-heat technique than in the high-heat technique because the investments generally employed with the low-heat technique may be denser.

The standardized hygroscopic technique was developed for alloys with a high gold content; the newer noble alloys may require slightly more expansion. This added expansion may be obtained by making one or more of the following changes:

- Increasing the water bath temperature to 40 °C
- Using two layers of liner
- Increasing the burnout temperature to a range of 600 to 650 °C

High-Heat Thermal Expansion Technique

This approach depends almost entirely on using a high-heat burnout to obtain the required expansion, while at the same time eliminating the wax pattern. Additional expansion results from the slight heating of gypsum investments on setting, thus expanding the wax pattern, and the water entering the investment from the

wet liner adds a small amount of hygroscopic expansion to the normal setting expansion.

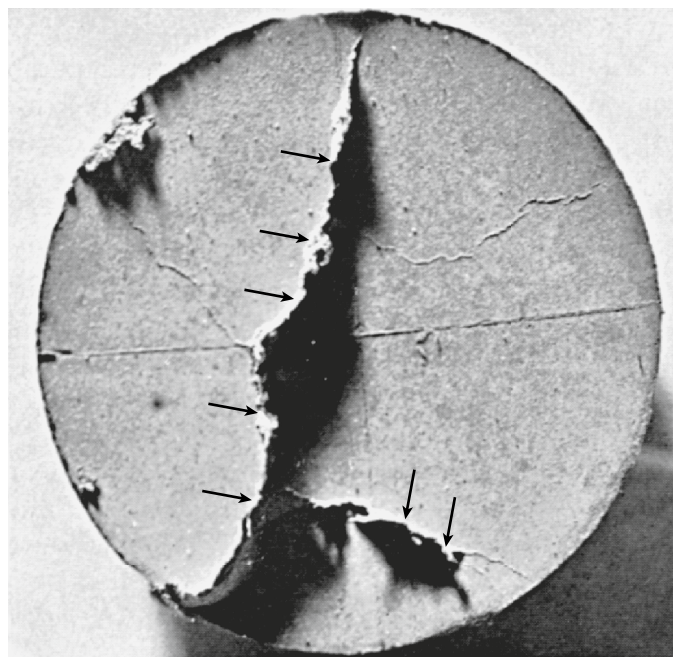
Casting Metal in Gypsum Investments

These casting investments are relatively fragile and require the use of a metal ring for protection during heating. The molds are usually placed in a furnace at room temperature, slowly heated to 650 to 700 °C in 60 minutes, and held for 15 to 30 minutes at the upper temperature.

The rate of heating has some influence on the smoothness and, in some instances, the overall dimensions of the investment. Initially, rapid heating can generate steam, which can cause flaking or spalling of the mold walls. Too many patterns in the same plane within the investment often cause separation of a whole section of investment. This is because the expanding wax creates excessive pressure over a large area.

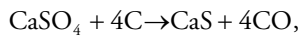
Too rapid of a heating rate may also cause cracking of the investment. In such a case, the outside layer of the investment expands much more than the center sections. Consequently, the outside layer starts to expand thermally, resulting in compressive stress in the outside layer, which counteracts tensile stresses in the middle regions of the mold. Such a stress distribution causes the brittle investment to crack from the interior outward in the form of radial cracks. These cracks, in turn, produce a casting with fins or spines like those shown in Figure 14-14. This condition is likely to be present with a cristobalite investment. The comparatively low inversion temperature of cristobalite and the rapid rate of expansion during inversion make it especially important to heat the investment slowly.

Breakdown of the dental investment and the resulting contamination and brittleness of the gold alloy casting probably occur more frequently than is generally realized. The mechanism of this investment decomposition and alloy contamination is related to a chemical reaction between the residual carbon and calcium sulfate binder. Calcium

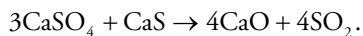


• **Figure 14-14** Fins (arrows) on the surface of a casting that formed as a result of cracks in the investment before casting of the metal.

sulfate per se does not decompose unless heated above 1000 °C. However, the reduction of calcium sulfate by carbon takes place rapidly above 700 °C, in accordance with the following reactions:



(3)



(4)

This reaction takes place whenever gypsum investments are heated above 700 °C in the presence of carbon. The sulfur dioxide as a product of this reaction contaminates gold castings and makes them extremely brittle. This fact emphasizes the need to eliminate the wax during heating.

After the casting temperature has been reached, the casting should be made immediately. Maintaining a high temperature for a considerable length of time may result in sulfur contamination of the casting and a rough surface on the casting because of the disintegration of the investment. To avoid this problem, some technicians use furnaces with heating elements on all four sides, thereby reducing the burnout time.

Despite all these precautions and reasons for using a slow burnout technique, the desire for rapid results has led to improved investment formulations. A few gypsum investments, some with a considerable amount of cristobalite, are now offered for use with a much more rapid burnout procedure. Some suggest placing the mold in a furnace at 315 °C for 30 minutes, and following this with very rapid heating to the final burnout temperature. In addition, a few investments may be placed directly into a furnace at the final burnout temperature, held for 30 minutes, and cast. Because of furnace design, the proximity of the mold to the heating element, and the availability of air in the muffle, the size and smoothness may be affected. It is advisable to consider these factors carefully before a casting is made in this manner.

Casting in Phosphate Investments

Phosphate investments obtain their expansion from the following sources:

1. Expansion of the wax pattern—This is considerable because the setting reaction raises the mold temperature substantially.
2. Setting expansion—This is usually higher than in gypsum investments, especially because special liquids may be used to increase such expansion.
3. Thermal expansion—This is greater when taken to temperatures higher than those used for gypsum-bonded investments.

A total expansion of 2% or more may be required for alloys used to produce metal-ceramic prostheses because these alloys have higher melting and solidification temperatures. Although phosphate investments are usually much harder and stronger than gypsum investments, they are nevertheless quite brittle and are subject to the same unequal expansion of adjacent sections, as phase changes occur during heating.

The usual burnout temperatures for phosphate-bonded investments range from 750 to 1030 °C. The highest temperatures are required for base-metal alloys. The heating rate is usually slow to 315 °C and is quite rapid thereafter, reaching completion after a hold at the upper temperature for 30 minutes. Most burnout furnaces are capable of being programmed for heating rates and holding times.

The procedure for investing a wax pattern in a phosphate-bonded investment is essentially the same as that for a gypsum-bonded investment. As previously mentioned, the working time can vary depending on the L/P ratio, special liquid concentration, temperature, mixing time, mixing rate, and operator skill and experience.

As with any investment that has a high thermal expansion, especially when marked changes in expansion or contraction occur, it is necessary to use a slow heating rate during burnout to prevent possible cracking or spalling. Most modern burnout furnaces are capable of being programmed for heating rates and holding times. For those that are not, it is advisable to use a two-stage burnout, holding at 200 to 300 °C for at least 30 minutes before completing the burnout. Recommendations for the rate of heating vary, so it is wise to follow the instructions for the specific investment used.

Although phosphate investments appear strong, they are still susceptible to disrupting influences during burnout. When the wax softens, it expands much more than does the investment. When investing, it is desirable to leave 3 to 6 mm of investment around each pattern and to stagger the patterns if several are placed in the same ring. Several patterns positioned along a plane can exert tremendous pressure and fracture almost any investment, but particularly the phosphate-bonded materials. The rapid expansion of cristobalite investment at approximately 300 °C requires slow heating to prevent fracture. After the temperature reaches 400 °C, the rate of heating can be safely increased. After burnout, usually at a final temperature of 700 to 1030 °C depending on the alloy melting range, the casting is made. The permeability of the phosphate investment is low compared with that of a gypsum-bonded investment. Therefore the required casting pressure is greater than that for a gypsum mold.

Recovery and cleaning of the casting are more difficult when a phosphate-bonded investment is used. Also, the particles usually include large grains of quartz. In some instances, such as with gold-containing alloys, the investment adheres rather tenaciously, usually requiring cleaning in an ultrasonic device. Neither the phosphate binder nor the silica refractory is soluble in HCl or H₂SO₄. Cold hydrofluoric acid (HF) dissolves the silica refractory quite well without damage to a gold-based or a palladium-silver alloy, but this acid must be used carefully with other alloys. Even dilute HF should not be used unless the necessary neutralizing solutions are immediately at hand and the clinician is familiar with the correct handling techniques. Caution: once the user's tissues are injured, the damage cannot be reversed. Alternative commercially available solutions can be used with greater safety. Base-metal alloys require a light grit-blasting, usually with fine alumina. Cobalt-chromium-based partial dentures are usually sandblasted to remove the investment. Acid should not be used for cleaning base-metal alloys.

The selection of the appropriate phosphate-bonded investment must be based on the composition of the alloy to be used. Carbon-containing investments are well suited for gold-based crown and bridge casting alloys and metal-ceramic alloys. However, if the alloy is carbon-sensitive (such as with Ag-Pd, high-Pd, Pd-Ag, Ni-Cr-Be, Ni-Cr, and Co-Cr alloys), a noncarbon investment should be used.

Because the entire process involving phosphate investments is lengthy, the demand for time-saving changes is strong. Investment manufacturers have answered this demand, resulting in the availability of investments that can be subjected to two-stage

heating more rapidly by being placed directly in the furnace at the top temperature, held for 20 to 30 minutes, and then cast. To save more time, manufacturers also offer ringless investment; no metal ring or liner is needed. However, a reusable plastic ring is still required during the investing procedure. The plastic ring is tapered so that once the investment has set, it can be pushed out of the ring, held for a specified time to ensure complete setting, and then placed directly into the hot furnace. Obviously, the expansion on setting for this method is different from that when a lined ring is used, and changes in overall fit must be considered. The required expansion may be adjusted by varying the liquid concentration.

Time Allowable for Casting

An investment contracts thermally as it cools after casting. When the thermal expansion or high-heat technique is used, the investment loses heat after the heated ring is removed from the furnace and the mold contracts. Because of the liner and the low thermal conductivity of the investment, a short time can elapse before the temperature of the mold is appreciably affected. Under average conditions of casting, approximately 1 minute can pass without a noticeable loss in dimension.

In the low-heat casting technique, the temperature gradient between the investment mold and the room is not as great as that employed with the high-heat technique. Also, the thermal expansion of the investment is not as important to the shrinkage compensation. However, the burnout temperature lies on a steep portion of the thermal expansion curve rather than on a plateau portion, as in the high-heat technique. Therefore in the low-heat

casting technique, the alloy should also be cast soon after removal of the ring from the oven; otherwise, a significant variation from the desired casting dimensions may occur.

Casting Machines

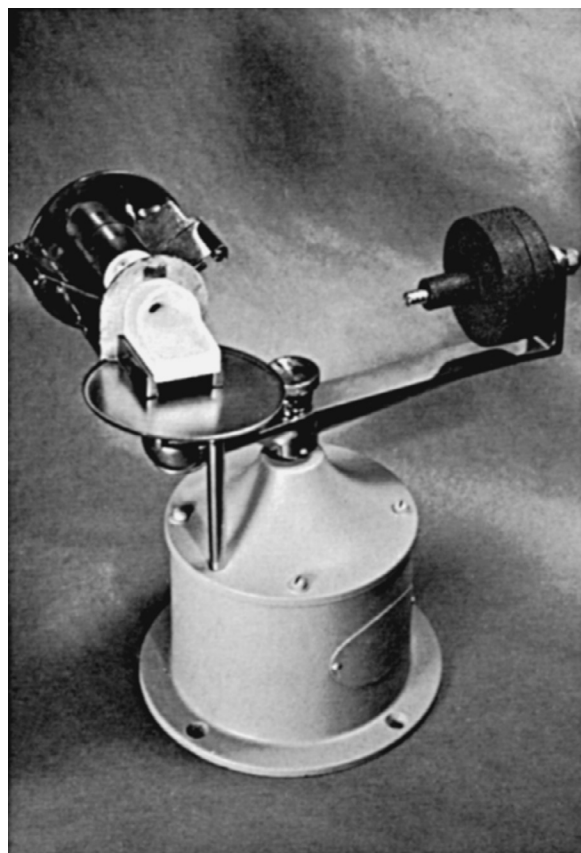
Each casting machine must perform two essential functions: metal melting and delivery of liquid metal to a casting ring. Metals can be melted by torch flame, electrical resistance heating, induction vacuum-arc, or laser beam. Liquid metal can be delivered by centrifuge, gravity, or vacuum or subjected to additional pressure to force the alloy into the mold. The following subsections describe four typical casting machines used in dentistry. It is important to follow the manufacturer's directions precisely for any of these devices.

Torch Melting/Centrifugal Casting Machine

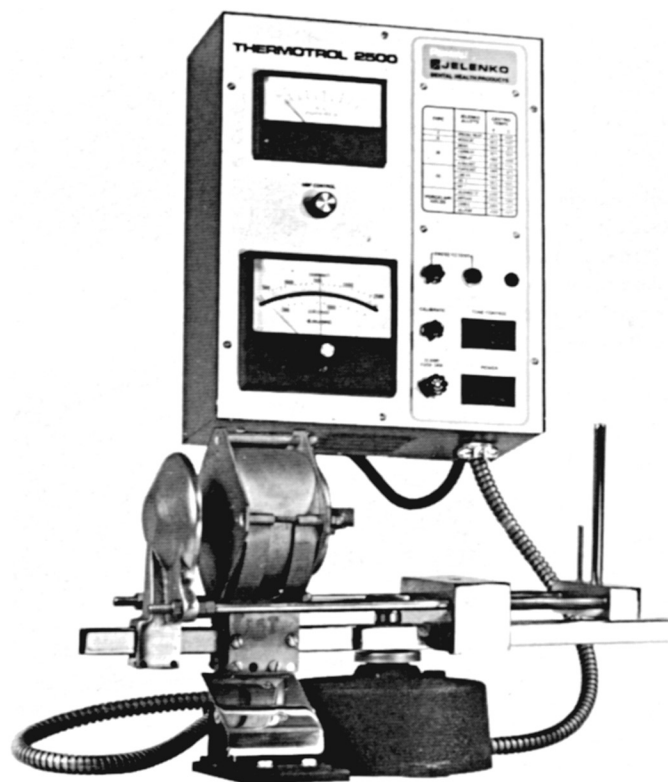
The casting-machine spring is first wound from two to five turns (depending on the alloy). The alloy is melted by a torch flame in a glazed ceramic crucible attached to the "broken arm" of the casting machine (Figure 14-15). The torch flame is generated from a gas mixture of propane and air, natural gas and air, acetylene and air, or acetylene and oxygen. Once the metal has reached the casting temperature and the heated casting ring is in position, the machine is released, and the spring initiates a rotational motion.

Electrical Resistance-Heated Casting Machine

In this device, current is passed through a resistance heating coil, melting the alloy in a graphite or ceramic crucible. The advantage of the design is that the crucible in the furnace is located flush against the casting ring (Figure 14-16). Therefore the alloy



• **Figure 14-15** Centrifugal casting machine, spring-wound.



• **Figure 14-16** Spring-wound casting machine with electrical resistance melting furnace.

remains molten slightly longer, again ensuring that solidification progresses completely from the tip of the casting to the button surface.

Induction Melting Machine

With this unit, the alloy is melted by an induction field that develops within a crucible surrounded by water-cooled metal tubing (Figure 14-17). The electric induction furnace is a transformer in which alternating current flows through the primary winding coil and generates a variable magnetic field in the location of the alloy to be melted in a crucible. Once the alloy reaches the casting temperature in air or in a vacuum, it is forced into the mold by centrifugal force, air pressure, or vacuum. Induction melting is more commonly used with base-metal alloys.

Direct-Current Arc Melting Machine

The direct-current arc is produced between two electrodes in an argon environment: the alloy and the water-cooled tungsten electrode. The temperature within the arc exceeds 4000 °C, and the alloy melts very quickly. However, this method poses a high risk of overheating the alloy, and damage may result after only a few seconds of prolonged heating. For titanium and titanium

alloys, vacuum arc heated-argon pressure casting machines are required.

Additional Variables Associated With Casting

Casting Crucibles

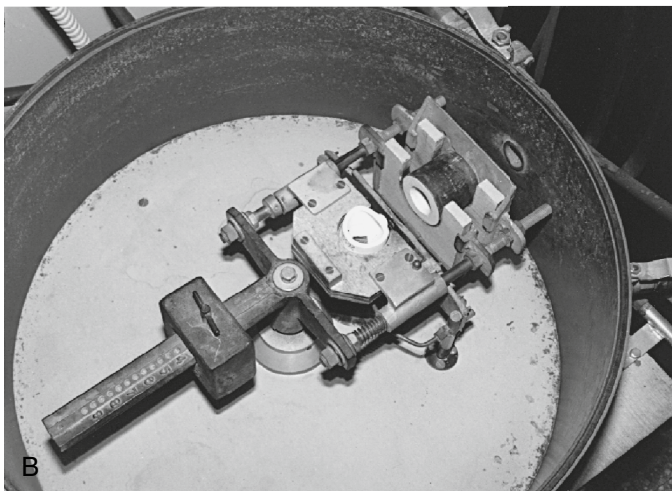
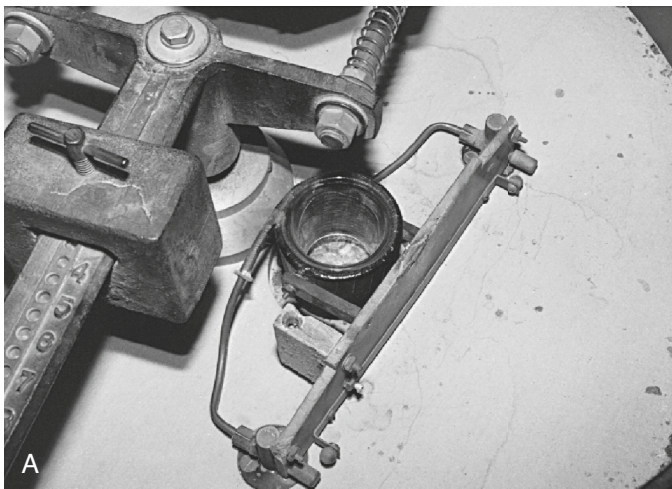
Generally, four types of casting crucibles are available: clay, carbon, quartz, and zirconia-alumina. Clay crucibles are appropriate for many of the crown and bridge alloys, such as the high-noble and low-noble types. Carbon crucibles can be used not only for high-noble crown and bridge alloys but also for the higher-fusing gold-based metal-ceramic alloys.

Crucibles made from alumina, quartz, or silica are recommended for high-fusing alloys of any type. These are especially suited for alloys that have a high melting temperature or those that are sensitive to carbon contamination. Crown and bridge alloys with a high palladium content, such as palladium-silver alloys for metal-ceramic copings and any of the nickel-based or cobalt-based alloys, are included in this category.

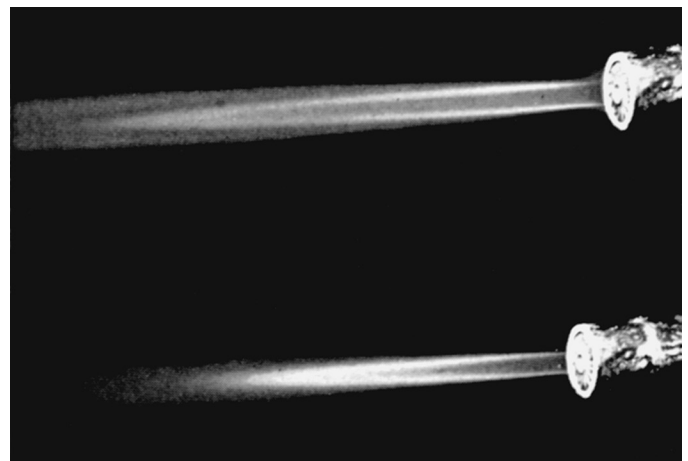
Torch Melting of Noble-Metal Alloy

Noble-metal alloy is best melted by placing it on the inner sidewall of the crucible. Thus the operator can better observe the progress of the melting, and there is a better opportunity for any gases in the flame to be reflected from the surface of the alloy rather than being absorbed.

The fuel used in most instances is a mixture of natural or artificial gas and air, although oxygen and acetylene combinations can also be used. The temperature of the gas-air flame is greatly influenced by the nature of the gas and the proportions of gas and air in the mixture. Care should be taken to obtain a nonluminous brush flame with the different combustion zones clearly differentiated. Two types of flames can be obtained with a casting torch, as shown in Figure 14-18. The air supply for the lower flame is excessive so that incomplete combustion and a lower temperature will result. This type of flame is likely to be favored by the beginner because the roaring sound that accompanies this flame adjustment “sounds” hot. The upper brush flame indicates the proper adjustment for maximal efficiency and temperature.



• **Figure 14-17** Induction melting casting machine. **A**, Water-cooled induction coil. **B**, Vertical crucible (white area) positioned within the induction coil.



• **Figure 14-18** Two types of nonluminous flames showing combustion areas. The upper flame should be employed for fusing noble-metal alloys. The lower flame results from too much air in the mixture.

The parts of the gas–air flame can be identified by the conical areas in [Figure 14-18](#). The first long cone emanating directly from the nozzle is the zone in which the air and gas are mixed before combustion. No heat is present in this zone. The next cone, which is green and immediately surrounding the inner cone, is known as the *combustion zone*. Here, the gas and air are partially burned. This zone is oxidizing and should always be kept away from the molten alloy during fusion.

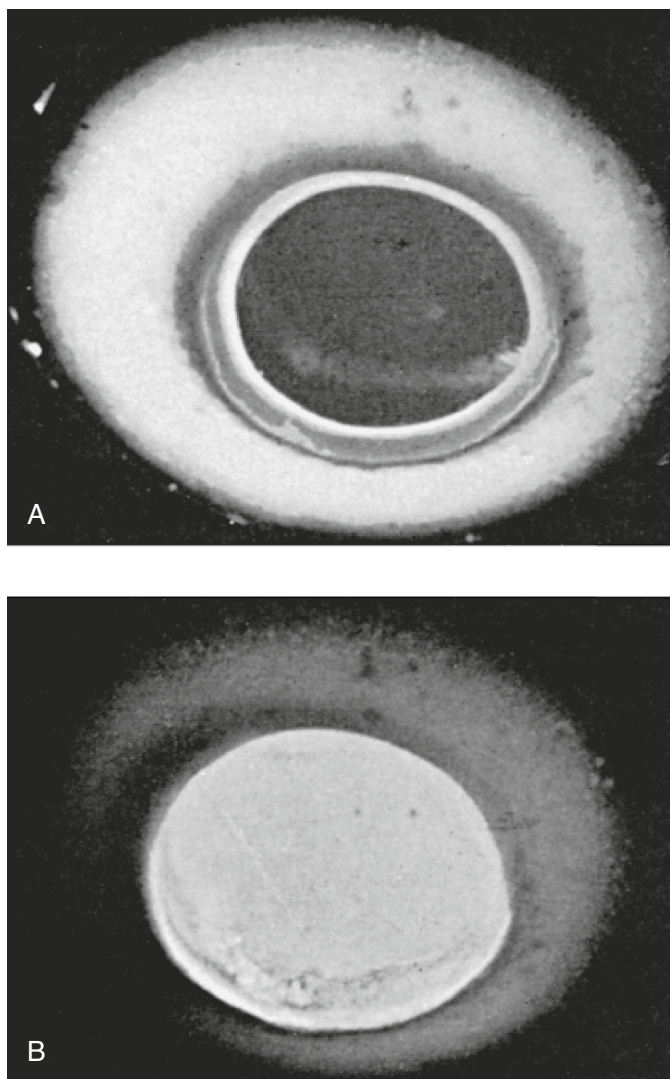
The next zone, dimly blue and located just beyond the tip of the green combustion zone, is the reducing zone. This is the hottest part of the flame, and it should be kept constantly on the alloy during melting. The outer cone (oxidizing zone) is the area in which combustion occurs with the oxygen in the air. Under no circumstances should this portion of the flame be used to melt the alloy. Not only is its temperature lower than that of the reducing zone, but it also oxidizes the alloy.

With a little practice, the technician or clinician can readily detect whether the proper zone of the flame is in contact with the metal by observing the condition of the alloy surface. When the reducing zone is in contact, the surface of the gold alloy is bright and mirrorlike, as indicated in [Figure 14-19, A](#). When the oxidizing portion of the flame is in contact with the alloy, a dull film of “dross” develops over the surface, as shown in [Figure 14-19, B](#). Although care should be taken not to overheat the alloy, there is generally more likelihood of underheating when the gas–air flame is used. The alloy first appears to be spongy, and then small globules of fused alloy appear. The molten alloy soon assumes a spheroidal shape, as indicated in [Figure 14-19, A](#). At the proper casting temperature, the molten alloy is light orange and tends to spin or follow the flame when the latter is moved slightly. At this point, the alloy should be approximately 38 to 66 °C above its liquidus temperature. The casting should be made immediately when the proper temperature is reached. As previously discussed, various devices are also available for melting the alloy electrically.

It is desirable to use a flux for gold crown and bridge alloys to aid in minimizing porosity. When properly used, the flux increases the fluidity of the alloy, and the film of flux formed on the surface of the molten alloy helps prevent oxidation, absorbs contaminants, and is left behind at the moment of casting. Reducing fluxes containing powdered charcoal are often used, but small bits of carbon may be carried into the mold and cause a deficiency at a critical margin. Although such reducing fluxes are excellent for cleaning old alloy, a better flux for the casting procedure may be made from equal parts of fused borax powder ground with boric acid powder. The boric acid aids in retaining the borax on the surface of the alloy. The flux is added when the alloy is completely melted and should be used with both old and new alloy. Old sprues and buttons from the same alloy may be recast if they are not contaminated.

Melting of Base Metals

Although torch melting can be used in some cases, most base metals of Ni–Cr, Ni–Cr–Be, Co–Cr, Co–Cr–Mo, Co–Ni–Cr, commercially pure Ti, and Ti–Al–V require special melting equipment, such as induction melting machines, vacuum melting devices, or arc melting units. The procedures required are designed to minimize the risk for excessive oxidation or an interaction of the molten alloys with the recommended casting investments. It is beyond the scope of this book to discuss these methods; the reader is referred to specialized instruction manuals developed by the manufacturers of these products.



• **Figure 14-19** Effect of the flame zone on melting. **A**, A mirrorlike surface of the metal indicates that the reducing zone of the flame is in contact with the metal. **B**, A cloudy surface indicates that the oxidizing portion of the flame is in contact with the metal surface oxidation because of improper positioning of the torch flame.

Cleaning the Casting

When a Type 3 or 4 gold alloy has been cast and has solidified, the ring should be quenched in water as soon as the button exhibits a dull-red glow. Two advantages are gained in quenching: (1) the noble-metal alloy is left in an annealed condition for burnishing, polishing, and similar procedures ([Chapter 2, Gold-Copper System](#)), and (2) when the water contacts the hot investment, a violent reaction ensues, resulting in a soft, granular investment that is more easily removed.

The surface of the casting often appears dark because of oxides and tarnish. Such a surface film can be removed by a process known as *pickling*, which consists of heating the discolored casting in an acid. Commonly used pickling solution for noble-metal alloys is a 30% HCl solution. The disadvantage of HCl is that the fumes from the acid are likely to corrode laboratory metal furnishings. In addition, these fumes are a health hazard and should be vented via a fume hood. However, the pickling process can be performed ultrasonically while the prosthesis is sealed in a Teflon

container. Commercial products based on phosphoric acid, sulfamic acid, and other acids are also available for pickling noble-metal prostheses.

The best method for pickling is to place the casting in a test tube or dish and pour the acid over it. It may be necessary to heat the acid, but boiling should be avoided because of the considerable amount of acid fumes involved. After pickling, the acid is poured off, and the casting is removed. The pickling solution should be renewed frequently because it is likely to become contaminated after reusing the solution several times.

In no case should the casting be held with metallic tongs, which can contaminate the casting when both the casting and the tongs are in contact in the pickling solution. The pickling solution usually contains small amounts of copper dissolved from previous castings. When the metallic tongs contact this electrolyte, a small galvanic cell is created, and copper may be deposited on the casting at the point where the tongs grip it. This copper deposition extends into the alloy and is a future source for discoloration in the area.

Gold- and palladium-based metal-ceramic alloys, and base-metal alloys, are generally not pickled if they are to be bench-cooled to room temperature before the casting is removed from the investment.

CRITICAL QUESTION

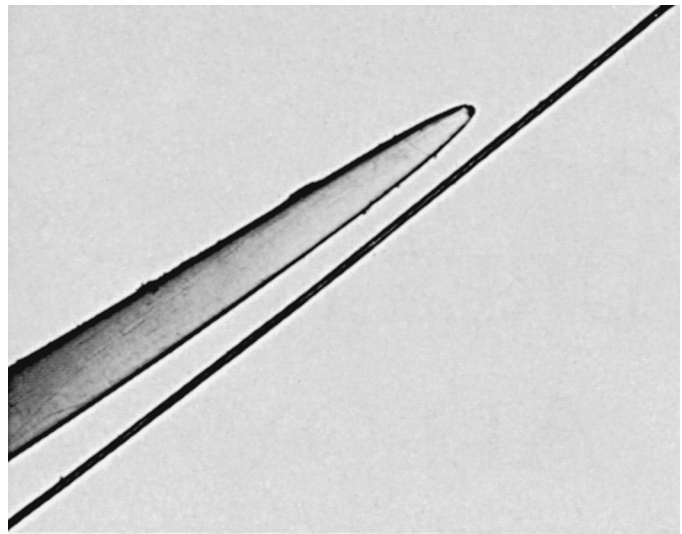
Why is the marginal fit of cast crowns on a prepared tooth essential to the long-term clinical success of metal prostheses?

Clinical Evaluation of Casting Fit

Dental castings can be produced in any size (from a denture base to the smallest inlay). The procedures employed for the construction of small restorations, such as inlays, onlays, crowns, and endodontic posts, are the primary topic of this chapter. The fundamental principles are the same, regardless of the size of the casting, and the techniques differ only in sprue design, type of investment, and method of melting the alloy.

The casting process is designed to provide a metallic duplication of missing tooth structure, with as much accuracy as possible. The tolerance limits for the fit and marginal adaptation of a cast restoration are not known. In a clinical study, 10 experienced dentists were asked to evaluate the marginal adaptation of a group of inlays, using a sharp dental explorer and radiographs. After the cemented restorations were graded, they were microscopically measured at the marginal openings of various areas. For “acceptable” restorations, the mean opening was 21 μm at the occlusal surface and 74 μm at the gingival region, which is not as accessible visually. There was little agreement among these 10 dentists on the acceptability of the marginal openings when evaluated by either dental explorers or radiographs.

The difficulty in detecting small discrepancies at the margins of cemented restorations is associated with the use of sharp dental explorers that have a relatively large radius of curvature at the tip compared with the width of margin gaps that are being evaluated. As shown in Figure 14-20, the tip of this unused new explorer may not “catch” a 60- μm margin gap, whose width is the diameter of a human hair, as it traverses along a path perpendicular to the gap. If this explorer tip substantially penetrates a gap during probing, the fit of a crown, inlay, or onlay will not be

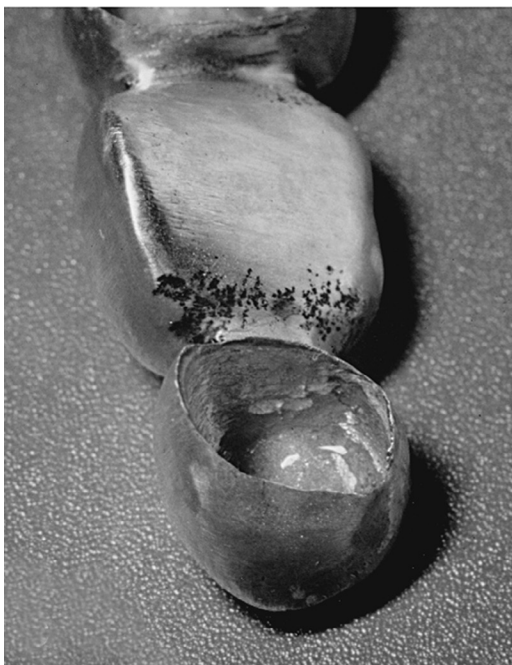


• **Figure 14-20** Cross section of an unused dental explorer tip (top) and a 60- μm hair ($\times 25$). (From McLean JW, van Fraunhofer JA: The estimation of cement film thickness by an in vivo technique, *Br Dent J* 131:107–111, 1971.)

clinically acceptable. This illustration poses the question of how readily a hairline gap can be detected by running an explorer over the margins of the restoration, especially in interdental areas that must often be probed at a small angle to the surface. It is obvious that the accuracy of the inlay or crown should be greater than can be detected by the eye or by the conventional methods of clinical testing. At the margins of the cemented restoration, a thin line of cement is always present, even though it may not be readily visible. Except for resin-based luting materials, the present dental cements are somewhat soluble and can deteriorate in the oral cavity over time. Thus the less accurate the casting fit and the greater the amount of cement exposed, the more likely it is that the cement will degrade. Certainly, a high degree of accuracy in marginal adaptation of 25 μm or less cannot be guaranteed for all cast restorations. It stands to reason that the more accurate the fit of the casting, the less the likelihood of leakage, plaque accumulation on the cement, and secondary caries will develop later.

Assuming that the wax pattern is satisfactory, the procedure then becomes a matter of enlarging the mold uniformly and sufficiently to compensate for the thermal casting shrinkage of the alloy. Theoretically, if the shrinkages of the wax and the alloy are known, the mold can be expanded enough to compensate for such shrinkage. Unfortunately, there are variables in the behavior of the materials and the wax that cannot be precisely controlled. The overall dimensional accuracy possible with current techniques has not been clearly defined. Thus neither the allowable tolerance of accuracy in the fit of the casting nor that obtainable during the casting procedure is known. In the final analysis, the casting procedure is partly empirical, and previous experience is very beneficial.

There are many steps in the procedure for which a considerable number of facts are known. In addition, certain variations in the techniques described here produce equally satisfactory results. However, any technique involves strict adherence to certain fundamental principles common to all metals. These are the fundamentals emphasized in the following discussion.



• **Figure 14-21** Localized shrinkage porosity in the pontic of a three-unit fixed partial denture caused by delayed solidification and lack of a chill-set sprue.

Causes of Defective Castings

Seldom is a defect in a casting attributable to factors other than the carelessness or ignorance of the operator. With present techniques, casting failures should be the exception, not the rule.

Defects in castings can be classified under four headings: (1) distortion, (2) surface roughness and irregularities, (3) porosity (Figure 14-21), and (4) incomplete or missing detail. In almost every instance, defects in castings can be avoided by strict observance of procedures governed by certain fundamental rules and principles.

Distortion

Any marked distortion of the casting is probably related to a distortion of the wax pattern, as described in Chapter 13, *Manipulation of Inlay Wax*. The setting and hygroscopic expansions of the investment may produce a nonuniform expansion of the walls of the pattern. The gingival margins are forced apart by the mold expansion, whereas the solid occlusal bar of wax resists expansion during the early stages of setting. Therefore distortion increases as the thickness of the pattern decreases. As would be expected, the lower the setting expansion of the investment, the less the distortion. Generally, this is not a serious problem, but it accounts for some of the unexplained inaccuracies that may occur in small castings.

Surface Roughness, Irregularities, and Discoloration

Surface roughness is defined as finely spaced surface imperfections whose height, width, and direction establish the predominant surface pattern. Surface irregularities are isolated

imperfections, such as nodules, that are not characteristic of the entire surface area. Excessive roughness or irregularities on the outer surface of the casting necessitate additional finishing and polishing.

Even under optimal conditions, the surface roughness of the casting is invariably somewhat greater than that of the wax pattern. The difference is probably related to the particle size of the investment, and its ability to reproduce the wax pattern in microscopic detail. With proper manipulative techniques, normal increased roughness in the casting should not be a major factor in dimensional accuracy. However, improper technique can lead to a marked increase in roughness and to the formation of surface irregularities.

Air Voids

Small nodules on a casting are caused by air bubbles that become attached to the pattern during or subsequent to the investing procedure. Such nodules can sometimes be removed if they are not in a critical area. However, for nodules on margins or on internal surfaces, the removal of these irregularities might alter the fit of the casting. As previously noted, the best method to avoid air bubbles is to use the vacuum investing technique. A wetting agent may be helpful in preventing the collection of air bubbles on the pattern surface, but it is by no means a certain remedy. As previously discussed, it is important that the wetting agent be applied in a thin layer. It is best to air-dry the wetting agent because any excess liquid dilutes the investment, possibly producing surface irregularities on the casting.

Water Films

If the wax pattern is slightly moved, jarred, or vibrated after investing or the painting of the investment does not result in intimate contact of the investment with the pattern, a water film may form irregularly over the surface. Occasionally, this type of surface irregularity appears as minute ridges or veins if the investment becomes separated from the wax pattern.

Liquid/Powder Ratio

The higher the L/P ratio, the rougher the casting. However, if too little water is used, the investment may be unmanageably thick so that it cannot be properly applied to the pattern. Air voids may not be sufficiently removed by vacuum investing.

Foreign Bodies

A rough crucible former with investment debris clinging to it may roughen the investment on its removal so that bits of investment are carried into the mold with the molten alloy. Contamination usually results not only in surface roughness but also in incomplete areas or surface voids.

Surface discoloration and roughness can result from sulfur contamination. An example of this effect may be seen in Figure 14-22, either from investment breakdown at elevated temperatures or from a high sulfur content of the torch flame.

Impact of Molten Alloy on the Mold Wall

Occasionally, the molten alloy may fracture or abrade the mold surface on impact, regardless of its bulk. Abrasion on the mold is reflected as a raised area on the casting that can prevent complete seating of the casting. A proper sprue to prevent the direct impact of the molten metal, at an angle of 90 degrees to the investment surface, reduces damage to the investment surface, and undesirable turbulence is avoided.

Pattern Position

When several patterns are invested in the same ring, they should not be placed too close together. The expansion of wax patterns before the investment sets can bring the patterns too close.

CRITICAL QUESTION

How can the risk of porosity and incomplete castings be minimized?

Porosity

Porosity may occur within the interior region of a casting that weakens the casting and extends to the external surface as roughness, which may also cause discoloration. There are two sources of porosity: solidification defects and trapped gases.

Continual feeding of molten metal through the sprue must occur to make up for the shrinkage of metal volume during solidification. If the sprue freezes in its cross section before this flow is completed, a localized shrinkage void will occur in the last portion of the casting that solidifies.

Four types of porosities are shown in [Figure 14-23, A & B](#): (1) localized shrinkage porosity, (2) microporosity, (3) pinhole porosity, and (4) subsurface porosity. Localized shrinkage generally

occurs near the sprue–casting junction, but it may occur anywhere between dendrites, as shown in [Figure 14-23, C](#), where the last part of the casting to solidify was between the dendrite branches as they developed.

Many alloys dissolve or occlude gases while they are molten. For example, both copper and silver dissolve oxygen in large amounts in the liquid state. Molten platinum and palladium have an affinity for hydrogen and oxygen. On solidification, the absorbed gases are expelled, and pinhole porosity results. The larger voids may also result from the same cause but also from gas that is mechanically trapped by the molten metal in the mold or by gas that is incorporated during the casting procedure. Larger spherical porosities can also be caused by gas occluded from a poorly adjusted torch flame or by the use of the mixing or oxidizing zones of the flame rather than the reducing zone. If the alloy has been used before, these types of porosities can be minimized by premelting the gold alloy in a graphite crucible or on a graphite block and correctly adjusting and positioning the torch flame during melting. The porosity that extends to the surface is usually in the form of small pinpoint holes. When the surface is polished, additional pinholes are uncovered.

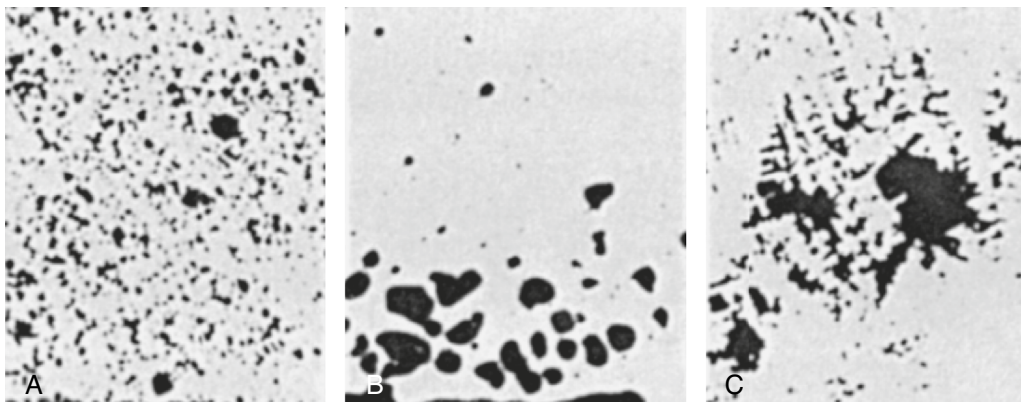
Subsurface porosity occurs on occasion, as shown in [Figure 14-23, B](#). The reasons for such voids are not well understood. They may be caused by the simultaneous nucleation of solid grains and gas bubbles at the first moment that the alloy freezes at the mold walls. This type of porosity can be diminished by controlling the rate at which the molten metal enters the mold.

Suck-back porosity may also occur externally, usually in the interior of a crown near the area of the sprue, if a hot spot has been created by the molten metal impinging from the sprue channel on a point of the mold wall. This hot spot causes the local region to solidify last and results in suck-back porosity, as shown in [Figure 14-24 \(left\)](#). Suck-back porosity often occurs at an occlusoaxial line angle or incisioaxial line angle that is not well rounded. This type of porosity defect can be eliminated by flaring the point of sprue attachment and reducing the mold–melt temperature differential—that is, lowering the casting temperature by about 30 °C. Such a result is shown on the right side of [Figure 14-24](#).

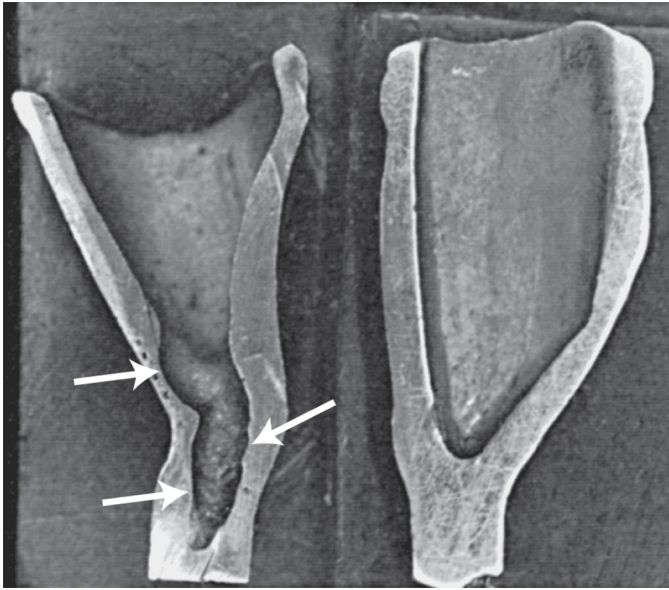
Entrapped air bubbles on the inner surface of the casting, sometimes referred to as *back-pressure porosity*, can produce large concave depressions such as those seen in [Figure 14-25](#). This is caused by the inability of the air in the mold to escape through the pores in the investment or by the pressure gradient that displaces the air pocket toward the end of the investment via the molten



• **Figure 14-22** A black-coated noble-metal alloy casting resulting from sulfur contamination or oxidation during alloy melting.



• **Figure 14-23** Localized porosities. **A**, Microporosity, pinhole porosity, and gas inclusions. Microporosity voids are irregular in shape, whereas the two other types tend to be spherical; the largest spherical voids are gas inclusions. **B**, Subsurface porosity. **C**, Localized shrinkage porosity. (Courtesy G. Ryge.)



• **Figure 14-24** Examples of suck-back porosity (*arrows on the left image*). The coping on the left was cast at 1370 °C. The coping on the right side was cast at 1340 °C. (Courtesy Dr. J. Nielsen.)



• **Figure 14-25** Surface irregularity on the cavity side of a casting caused by back-pressure porosity.

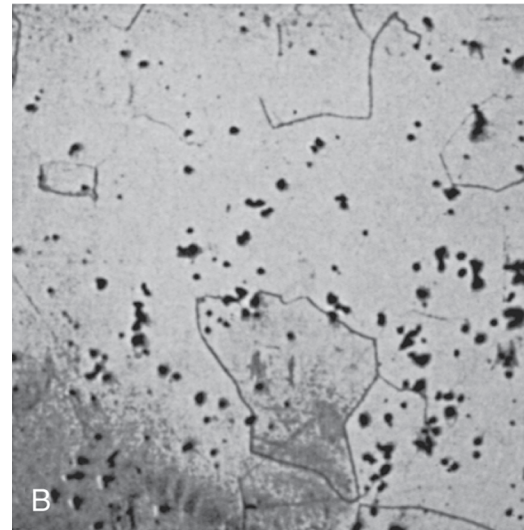
sprue and button. The incidence of entrapped air can be increased by the use of the dense modern investments.

All castings probably contain a certain amount of porosity, as exemplified by the photomicrographs shown in [Figure 14-26](#). This should be minimized because it may adversely affect the physical properties of the casting. Proper burnout, an adequate mold and casting temperature, a sufficiently high casting pressure, and a proper investment L/P ratio can minimize or eliminate entrapped-air porosity. It is good practice to make sure that the thickness of investment between the tip of the pattern and the end of the ring is not greater than 6 mm ([Figure 14-2](#)).

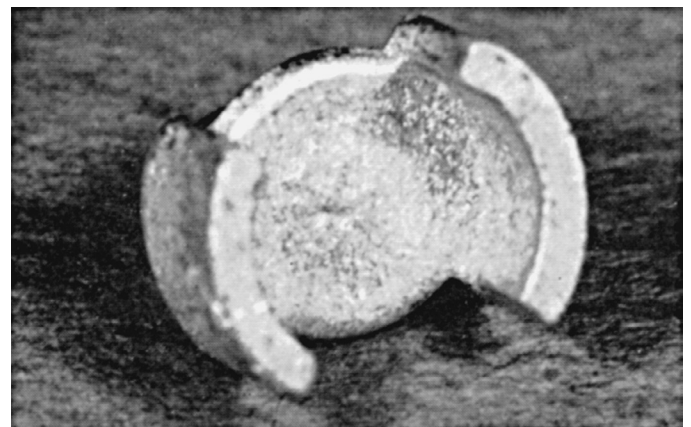
Incomplete Casting

Occasionally, the molten alloy may be prevented from completely filling the mold because of insufficient venting of the mold and high viscosity of the melted metal.

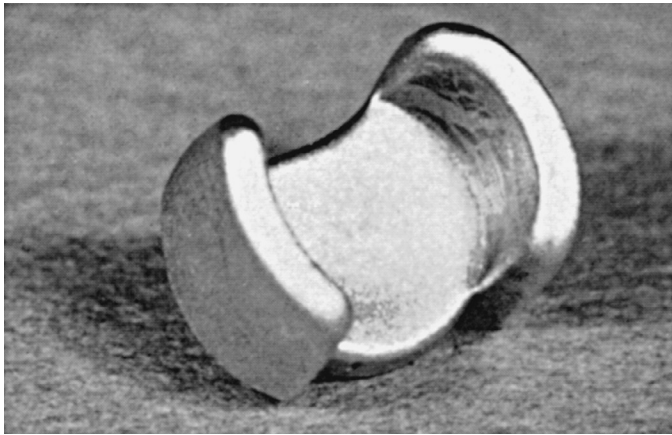
Insufficient venting is directly related to the back pressure exerted by the air in the mold. These failures are usually exemplified by rounded, incomplete margins ([Figure 14-27](#)). If the air



• **Figure 14-26** **A**, Grain structure of an as-cast American Dental Association (ADA) type III noble-metal alloy. **B**, Same alloy after a homogenization heat treatment at 725 °C for 70 minutes. Pinhole porosity is visible. (Courtesy B. Hedegard.)



• **Figure 14-27** Rounded, incomplete margins are evidence of insufficient casting pressure.



• **Figure 14-28** An incomplete casting resulting from incomplete wax elimination is characterized by rounded margins and a shiny appearance.

cannot be vented quickly through the investment, the molten alloy cannot fill the mold before it solidifies. The magnitude of the casting pressure should be suspected. Casting pressure should be maintained a few seconds longer to prevent back pressure during the early stage of solidification.

Residues from incomplete elimination of wax or plastic sprue may fill the pores in the investment so that the air cannot be vented completely. An example of a casting failure caused by incomplete wax elimination is shown in [Figure 14-28](#) and shown schematically in [Figure 14-29](#). Compared with [Figure 14-27](#), the shining appearance of [Figure 14-28](#) is caused by the strong reducing atmosphere of carbon monoxide left by residual wax.

Casting alloys exhibit varying viscosities and surface tensions in the molten state, depending on composition and temperature. Both the surface tension and the viscosity of a molten alloy decrease with temperature increases. Therefore the temperature of the alloy should be raised higher than its liquidus temperature so that its viscosity and surface tension are reduced so that the metal does not solidify prematurely as it enters the mold.

Suggested Readings

Earnshaw R: The effect of casting ring liners on the potential expansion of a gypsum-bonded investment, *J Dent Res* 67:1366–1370, 1988.

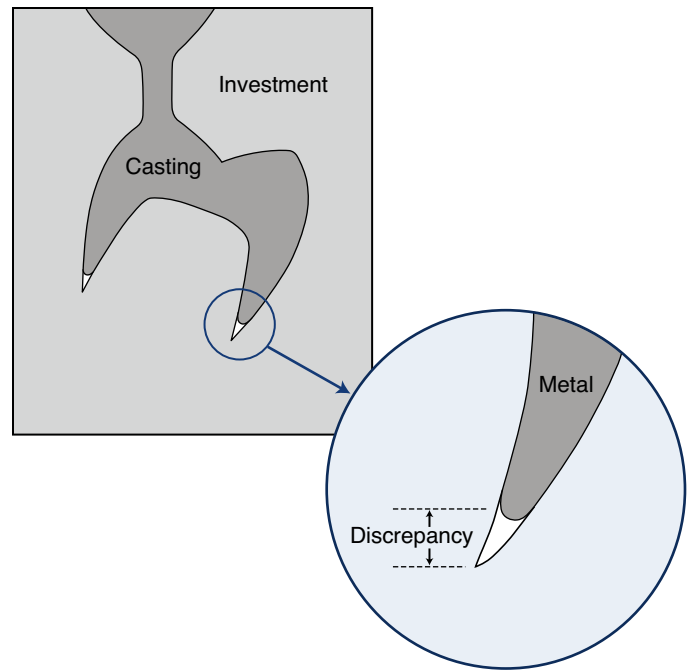
Total expansion, setting expansion, and thermal expansion of the investment setting against a smooth dry surface was 1.7%; against a dry ceramic liner, 1.6% to 1.7%; and against wet cellulose or wet asbestos, 2.2% to 2.3%. The ceramic liner can be used wet if it is treated with a surfactant instead of water.

Ito M, Yamagishi T, Oshida Y, et al: Effect of selected physical properties of waxes on investments and casting shrinkage, *J Prosthet Dent* 75:211–216, 1996.

This study evaluated the relationship between properties of paraffin and dental inlay waxes to casting shrinkage when patterns were invested with a phosphate-bonded investment. Casting shrinkage decreased as the flow of the wax pattern increased. If a low-flow wax or thick pattern is used, the size of the casting ring should be increased.

Jorgensen KD, Ono T: Distortion of wax crowns, *Scand J Dent Res* 92:253–256, 1984.

Distortion of wax crowns is enough to reduce the fit of the final restoration to a degree that is clinically unacceptable. This study



• **Figure 14-29** Schematic illustration of an incomplete casting.

Other Causes

Certain surface discolorations and roughness may not be evident when the casting is completed but may appear during service. For example, various gold alloys—such as brazing alloys (solders), bits of wire, and mixtures of different casting alloys—should never be melted together and reused for patient castings. The resulting mixture would form different phases that do not possess the proper physical properties needed and might form a eutectic phase with low corrosion resistance and discoloration.

suggests that wax pattern distortion may be minimized only by use of a pattern/die investing technique.

Neiman R, Sarma AC: Setting and thermal reactions of phosphate investments, *J Dent Res* 59:1478–1485, 1980.

The authors concluded that setting took place through the complex formation of $[\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}]_n$, excess reactants, and water, and that dehydration and thermal reactions led to a sequence of reactions resulting in the formation of $[\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}]$, $[\text{Mg}_2\text{P}_2\text{O}_7]_n$, $\text{Mg}_2\text{P}_2\text{O}_7$, and $\text{Mg}_3[\text{PO}_4]_2$.

Nomura GT, Reisbick MH, Preston JD: An investigation of epoxy resin dies, *J Prosthet Dent* 44:45–50, 1980.

In a comparison of three epoxy die materials with a type IV stone, full crown epoxy dies were undersized, MOD onlay resin dies were accurate, and detail reproduction was found to be comparable to the type IV gypsum. However, only one epoxy material had a hardness approaching that of the dental stone.

Pieralini AR, Benjamin CM, Ribeiro RF, et al: The effect of coating patterns with spinel-based investment on the castability and porosity of titanium cast into three phosphate-bonded investments, *J Prosthodont* 19:517–522, 2010.

The results show that investing technique with coating increased the castability for all phosphate-bonded investments.

Santos JF, Ballester RY: Delayed hygroscopic expansion of phosphate-bonded investments, *Dent Mater* 3:165–167, 1987.

Delayed hygroscopic expansion occurs when the investment is immersed in water after setting. Increased time of immersion and an increase in the special liquid concentration increased the hygroscopic setting expansion.

Taggart WH: A new and accurate method of making gold inlays, *Dent Cosmos* 49:1117–1121, 1907.

The dental “lost wax” process was developed by Taggart, opening the opportunity to cast accurate restorations in an investment mold.

Tourah A, Moshaverinia A, Chee WW: Effects of setting under air pressure on the number of surface pores and irregularities of dental investment materials, *J Prosthet Dent* 111:150–153, 2014.

Specimens set under positive pressure in a pressure chamber presented fewer surface bubbles than specimens set under atmospheric pressure. Positive pressure is effective and, therefore, is recommended for both gypsum-bonded and phosphate-bonded investment materials.

Zeltser C, Lewinstein I, Grajower R: Fit of crown wax patterns after removal from the die, *J Prosthet Dent* 53:344–346, 1985.

The effects of loading wax patterns before investment was determined. Repetitive loading revealed that the plastic deformation in wax was less after the second loading than after the first cycle for a specific load.

Selected Readings (Web Version)

Christensen GJ: Marginal fit of gold inlay castings, *J Prosthet Dent* 16:297–305, 1966.

In this laboratory study, 10 dentists accepted cemented gold inlays with a mean occlusal margin opening of 21 μm [range of 2 to 51 μm], a mean proximal margin opening of 26 μm [range of 9 to 34 μm], and a gingival margin opening of 74 μm [range of 34 to 119 μm]. Explorer examination of visually accessible areas was superior to either explorer or radiographic examination of visually inaccessible areas.

Cooney JP, Caputo AA: Type III gold alloy complete crowns cast in a phosphate-bonded investment, *J Prosthet Dent* 46:414–419, 1981.

Marginal fit was superior for castings made in phosphate-bonded investment; surface roughness was less when cast in the gypsum-bonded investment.

Da Silva LJ, Leal MB, Valente MLC, et al: Effect of casting atmosphere on the marginal deficiency and misfit of Ni-Cr alloys with and without beryllium, *J Prosthet Dent* 118:83–88, 2017.

Four casting conditions were investigated: flame-torch, induction/argon, induction/air, and induction/vacuum. The results demonstrated that beryllium-containing alloys cast in an argon atmosphere exhibited reduced marginal deficiency, and improved marginal adaptation could also be achieved by the torch technique.

Dootz ER, Asgar K: Solidification patterns of single crowns and three-unit bridge castings, *Quint Dent Technol* 10:299–305, 1986.

Solidification rates and patterns differed for type III gold alloy and a palladium-silver alloy. The gold alloy solidified in a random pattern, whereas the palladium-silver metal-ceramic alloy solidified in a unidirectional manner.

Eames WB, O'Neal SJ, Monteiro J, et al: Techniques to improve the seating of castings, *J Am Dent Assoc* 96:432–437, 1978.

Die spacing was the most suitable method to compensate for casting variables and to ensure improved marginal adaptation while also increasing retention by 25%.

Earnshaw R: The effect of casting ring liners on the potential expansion of a gypsum-bonded investment, *J Dent Res* 67:1366–1370, 1988.

Total expansion, setting expansion, and thermal expansion of the investment setting against a smooth dry surface was 1.7%; against a dry ceramic liner, 1.6% to 1.7%; and against wet cellulose or wet asbestos, 2.2% to 2.3%. The ceramic liner can be used wet if it is treated with a surfactant instead of water.

Finger W: Effect of the setting expansion of dental stone upon the die precision, *Scand J Dent Res* 88:159–160, 1980.

The addition of potassium sulfate and borax to type IV gypsums reduced setting expansion without affecting the physical properties.

Finger W, Ohsawa M: Accuracy of cast restorations produced by a refractory die-investing technique, *J Prosthet Dent* 52:800–803, 1984.

By minimizing distortion of the wax pattern, the refractory die-investing procedure can produce consistently accurate cast gold alloy restorations.

Hansen P: Predictable casting for dimensional shrinkage of fast-cast post-and-cores, *Oper Dent* 39:367–373, 2014.

The use of a phosphate investment with an accelerated technique was found to produce consistent and predictable shrinkage of cast post-and-cores.

Haralur SB, Hamdi OA, Al-Shahrani AA, et al: The effect of casting ring liner length and prewetting on the marginal adaptation and dimensional accuracy of full crown castings, *J Int Soc Prev Community Dent* 7:52–57, 2017.

This study shows that the dry cellulose ring liners provides better marginal adaptation in comparison to prewet cellulose ring liners, and accurate cuspal height was obtained with shorter ring liner in comparison to full-length cellulose ring liners.

Ito M, Kuroiwa A, Nagasawa S, et al: Effect of wax melting range and investment liquid concentration on the accuracy of a three-quarter crown casting, *J Prosthet Dent* 87:57–61, 2002.

Two phosphate-bonded investment mixtures were prepared: 100% special liquid and 75% special liquid. Casting shrinkage was smaller with the use of 100% special liquid. The casting shrinkage increased when waxes with a higher softening temperature were used.

Ito M, Yamagishi T, Oshida Y, et al: Effect of selected physical properties of waxes on investments and casting shrinkage, *J Prosthet Dent* 75:211–216, 1996.

This study evaluated the relationship between properties of para-fin and dental inlay waxes to casting shrinkage when patterns were invested with a phosphate-bonded investment. Casting shrinkage decreased as the flow of the wax pattern increased. If a low-flow wax or thick pattern is used, the size of the casting ring should be increased.

Jorgensen KD, Okamoto A: Restraining factors affecting setting expansion of phosphate-bonded investments, *Scand J Dent Res* 94:178–181, 1986.

The authors suggest that setting expansion is a highly unreliable means to compensate partially for the thermal contraction of casting alloys.

Jorgensen KD, Ono T: Distortion of wax crowns, *Scand J Dent Res* 92:253–256, 1984.

Distortion of wax crowns is enough to reduce the fit of the final restoration to a degree that is clinically unacceptable. This study suggests that wax pattern distortion may be minimized only by use of a pattern/die investing technique.

Junner RE, Stevens L: Anisotropic setting expansion of phosphate-bonded investment, *Aust Dent J* 31:434–439, 1986

In this study, the vertical setting expansion was significantly greater than the horizontal expansion in a rigid ring with liners. A flexible ring offered little restriction to horizontal expansion, reducing mold distortion.

Kalavathi M, Sachin B, Prasanna BG: Accuracy of castings fabricated with ringless casting investment system and metal ring casting investment system: A comparative study, *J Contemp Dent Pract* 17:165–170, 2016.

The study shows that ringless casting technique had produced better marginal accuracy compared with conventional casting technique.

Kanitkar AA, Kanitkar AS, Sasane RS, et al: Analyse the effect of different investment techniques and pattern materials on surface roughness of raw Ni-Cr castings—an in vitro study, *J Indian Prosthodont Soc* 20:97–103, 2020.

Wax patterns and resin patterns invested under increased pressure produce smoother casting surface than those invested at atmospheric pressure.

Kaplan J, Newman SM: Accuracy of the divestment casting technique, *Oper Dent* 8:82–87, 1983.

These investigators found that castings made using the divestment procedure fit more accurately than did castings made using a conventional stone-die and gypsum-bonded refractory investment technique.

Lautenschlager EP, Harcourt JK, Ploszaj LC: Setting reaction of gypsum materials investigated by x-ray diffraction, *J Dent Res* 48:43–48, 1969

An early study of the conversion from calcium sulfate hemihydrate to calcium sulfate dihydrate.

Leal MB, Pagnano VO, Bezzon OL: Effect of investment type and mold temperature on casting accuracy and titanium-ceramic bond, *Braz Dent J* 24:40–46, 2013.

For casting accuracy, expressed by marginal deficiency in micron, there is a difference between investment materials used, and the increase in temperature resulted in different effects for the tested investments.

Mackert JR, Jr: An expert system for analysis of casting failures, *Int J Prosthodont* 1:268–280, 1988.

An expert system was proposed for the diagnosis of common lost-wax casting problems, based on an interactive consultation session at a PC station, during which the user answered questions about defective castings. The computer responded with conclusions on the most likely cause of each problem.

- Mahler DB, Ady AB: An explanation for the hygroscopic setting expansion of dental gypsum products, *J Dent Res* 39:578, 1960.
A classic publication on the theory of hygroscopic setting expansion. An excellent reference for those interested in the mechanics of this phenomenon.
- Martin KH: An investigation of the effect of the water/powder ratio on the accuracy of the fit of gold alloy castings, *Aust Dent J* 1:202–203, 1956.
Use of the correct water/powder ratio with a gypsum investment is essential to obtain a good fit of castings, especially when the low-heat technique is used.
- Matsuya S, Yamane M: Decomposition of gypsum-bonded investments, *J Dent Res* 60:1418–1423, 1981.
At 900 °C, decomposition of gypsum-bonded investments occurred, leading to the formation of CaSiO_3 and Ca_2SiO_4 .
- Mueller HJ, Reyes W, McGill S: Surfactant-containing phosphate investment, *Dent Mater* 2:42–44, 1986.
The addition of surfactants in a phosphate-bonded casting investment can increase the hygroscopic setting expansion. The surfactant also makes the unset investment more viscous and reduces the compressive strength.
- Naylor WP, Moore BK, Phillips RW: A topographical assessment of casting ring liners using scanning electron microscopy (SEM), *Quint Dent Technol* 11:413–420, 1987.
Three types of nonasbestos ring liners exist: ceramic, cellulose, and a ceramic-cellulose combination. A liner containing an aluminosilicate component has the potential to produce respirable-size ceramic particles.
- Neiman R, Sarma AC: Setting and thermal reactions of phosphate investments, *J Dent Res* 59:1478–1485, 1980.**
The authors concluded that setting took place through the complex formation of $[\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}]_n$, excess reactants, and water, and that dehydration and thermal reactions led to a sequence of reactions resulting in the formation of $[\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}]$, $[\text{Mg}_2\text{P}_2\text{O}_7]_n$, $\text{Mg}_2\text{P}_2\text{O}_7$, and $\text{Mg}_3[\text{PO}_4]_2$.
- Nielsen JP: Pressure distribution in centrifugal dental casting, *J Dent Res* 57:261–269, 1978.
This article discusses the factors contributing to the pressure gradient that develops along the length of a casting in a centrifugal casting machine.
- Nielsen JP, Ollerman R: Suck-back porosity, *Quint Dent Technol* 1:61–65, 1976.
Using a gold-palladium-silver alloy with different sprue former lengths, diameters, and angles of attachment, lower casting temperature and flaring of the sprue former reduced suck-back porosity. The authors postulated that a “hot spot” is created in the mold that causes this type of porosity.
- Nomura GT, Reisbick MH, Preston JD: An investigation of epoxy resin dies, *J Prosthet Dent* 44:45–50, 1980.
In a comparison of three epoxy die materials with a type IV stone, full crown epoxy dies were undersized, MOD onlay resin dies were accurate, and detail reproduction was found to be comparable to the type IV gypsum. However, only one epoxy material had a hardness approaching that of the dental stone.
- Otun A, Lee H, Geminiani A, et al: Ring liner and burn-out temperature affect the clinical time required to fit a cast post, *J Prosthet Dent* 102:224–228, 2009.
Investing a post pattern without a ring liner and setting a lower final burn-out temperature yield cast posts that require significantly less adjustment time for clinical placement.
- Pieralini AR, Benjamin CM, Ribeiro RF, et al: The effect of coating patterns with spinel-based investment on the castability and porosity of titanium cast into three phosphate-bonded investments, *J Prosthodont* 19:517–522, 2010.**
The results show that investing technique with coating increased the castability for all phosphate-bonded investments.
- Prasad R, Al-Keraif AA, Kathuria N, et al: Accuracy of ringless casting and accelerated wax-elimination technique: a comparative in vitro study, *J Prosthodont* 23:157–162, 2014.
The ringless investment technique can produce castings with higher accuracy and can be favorably combined with the accelerated wax-elimination method.
- Saber FS, Abolfazli N, Mahboub F, et al: The effect of occlusal surface relief of dies on marginal adaptation of metal-ceramic casting copings, *J Prosthodont* 22:287–291, 2013.
Leaving the occlusal part of the die uncovered with the die spacer during investing procedure improved the crown seating considerably in the occlusal surface, as well as shoulder and bevel margins.
- Santos JF, Ballester RY: Delayed hygroscopic expansion of phosphate-bonded investments, *Dent Mater* 3:165–167, 1987.**
Delayed hygroscopic expansion occurs when the investment is immersed in water after setting. Increased time of immersion and an increase in the special liquid concentration increased the hygroscopic setting expansion.
- Smith CT, Diefenderfer KE: A direct refractory die technique for cast gold restorations, *Oper Dent* 42:122–132, 2017.
This article demonstrates a laboratory technique in which the final restoration is cast directly on the refractory die without removing the wax pattern.
- Steinbock AF: An overview of dental waxes, *Dental Lab News*, 1989 50 July.
- Stevens L: The effect of early heating on the expansion of a phosphate-bonded investment, *Aust Dent J* 28:366–369, 1983.
The thermal expansion of a phosphate-bonded investment decreased as heating was delayed from 1 to 6 hours after mixing. The setting expansion increased as the special liquid replaced water for mixing.
- Taggart WH: A new and accurate method of making gold inlays, *Dent Cosmos* 49:1117–1121, 1907.**
The dental “lost wax” process was developed by Taggart, opening the opportunity to cast accurate restorations in an investment mold.
- Tourah A, Moshaverinia A, Chee WW: Effects of setting under air pressure on the number of surface pores and irregularities of dental investment materials, *J Prosthet Dent* 111:150–153, 2014.**
Specimens set under positive pressure in a pressure chamber presented fewer surface bubbles than specimens set under atmospheric pressure. Positive pressure is effective and, therefore, is recommended for both gypsum-bonded and phosphate-bonded investment materials.
- Vaidyanathan TK, Schulman A, Nielsen JP, et al: Correlation between macroscopic porosity location and liquid metal pressure in centrifugal casting technique, *J Dent Res* 60:59–66, 1981.
Radiographic analysis revealed that the porosity is dependent on the location at which the sprue is attached to the casting. The location of the macroscopic porosity, at portions of the casting close to the free surface of the button, is dependent on the pressure gradient and therefore different heat transfer rates in different portions of the casting.
- Verrett RG, Duke ES: The effect of sprue attachment design on castability and porosity, *J Prosthet Dent* 61:418–424, 1989.
Flared and straight sprue attachments optimized castability and minimized porosity.
- Zeltser C, Lewinstein I, Grajower R: Fit of crown wax patterns after removal from the die, *J Prosthet Dent* 53:344–346, 1985.**
The effects of loading wax patterns before investment was determined. Repetitive loading revealed that the plastic deformation in wax was less after the second loading than after the first cycle for a specific load.

15

Digital Technology in Dentistry

OUTLINE

Intraoral Digital Scanner

Prototyping Tools

Diagnostic Systems

The Future

KEY TERMS

Additive manufacturing (AM) A process of constructing objects where material is incrementally added according to a computer-aided design (CAD) file; also known as *three-dimensional (3-D) printing*.

Augmented reality (AR) A form of virtual reality in which interacting with the real world is through simulation.

Computer-aided design (CAD) A computer technology that designs an object and creates a computer file for manufacture of the design.

Computer-aided manufacturing (or milling) (CAM) The use of software and computer-controlled machinery to automate a manufacturing process.

Cone-beam computed tomography (CBCT) An x-ray three-dimensional (3-D) imaging technology in which the radiation is divergent and forms a cone.

Digital An electronic technology that records or stores information in the form of binary digits (i.e., 1 and 0) or technology characterized by electronic and computerized devices (e.g., digital images).

Digital impression A virtual scan (digital model) of a patient's dentition and other structures that is generated with laser or

other optical scanning devices and converted into a digital format.

Fused deposition modeling (FDM) A three-dimensional (3-D) printing process that uses a continuous filament of a thermoplastic material; also known as *fused filament fabrication (FFF)* or *filament freeform fabrication*.

Prototyping The creation, modification, and optimization of two-dimensional or three-dimensional models of objects, which may be the final desired object or an interim object for examination of fit.

Quantitative light-induced fluorescence (QLF) A nondestructive diagnostic method for the detection and assessment of early carious lesions.

Subtractive manufacturing (SM) A process of making 3D objects by successively removing material from a solid block of metal, ceramic, polymer, or composite using computer-aided standard machining processes, such as turning, drilling or milling.

Virtual reality (VR) A computer-generated simulation that allows for interactive experiences.

Digital dentistry is the use of dental technologies or devices that incorporate digital or computer-controlled components to carry out dental procedures rather than using materials and mechanical or electrical tools. The use of digital dentistry can make carrying out dental procedures more efficient than the use of mechanical tools. A variety of digital devices, such as intraoral and facial scanners, **cone-beam computed tomography (CBCT)**, software for **computer-aided design (CAD)** and **computer-aided manufacturing (or milling) (CAM)**, and three-dimensional (3-D) printing provide new potential alternatives to replace the manual tasks and improve the quality of care and patient experiences. These technologies have several advantages, including accurate and time-saving measurement, electronic storage, and file transmission to automate processes.

CRITICAL QUESTION

How are digital impressions made, and what are their applications in dentistry?

Intraoral Digital Scanner

Intraoral scanner/cameras, similar in size to a dental mirror, are able to show tooth surfaces in 3-D rather than two-dimensional (2-D) photographic images. Such cameras are used in the dental office, without the help of a dental technician. The clear images enable color matching, diagnostic tasks, orthodontic and implant placement, and **digital impressions**.

Digital Impressions

Intraoral scanners use light to create accurate 3-D records of the dental arches, using only a beam of infrared light, that are digitally recorded. Such digital impressions almost instantly re-create the positive impression of a patient's dentition and other structures in a digital format. In contrast, conventional impressions require placing a tray of impression material over the dental arches to create an intaglio of the dentition, from which a positive model must be made.

Digital impression techniques are a clinically acceptable alternative to conventional impression methods in the fabrication of crowns and short fixed dental prostheses (FDPs) and implant-supported crowns. Digital impressions are faster, are more comfortable for patients, and shorten chair time. However, digital impressions are currently less accurate for full-mouth and edentulous-jaw impressions.

Color Matching

A physical shade guide is the traditional means of matching a patient's teeth to restorative materials. However, differences often occur in shade matching as a result of variations among observers (dentist, technician, patient) and sources of illumination. Digital cameras have improved both dental laboratory communication and patient satisfaction. Such images are needed for the selection of materials, as discussed in the CAM section that follows.

CRITICAL QUESTIONS

What is prototyping?

What are subtractive and additive processes, and what are their relative advantages and disadvantages?

Prototyping Tools

Prototyping technology is based on using computer software and systems to assist in the creation, modification, analysis, and optimization of 2-D or 3-D models of objects. Any computer program that includes computer graphics and engineering functions for manipulation can be classified as CAD software. CAM in dentistry is the construction of a restorative device using the output from the CAD software. CAM may be additive (buildup of a material) or subtractive (removal of material from a larger starting piece).

CRITICAL QUESTION

Which dental applications can be used with CAD-CAM technology?

Indications for CAD-CAM

Many indications and materials are available for chairside CAD-CAM restorations, as shown in the list that follows. Each type of material offers unique features for its indications. The CAD-CAM system represents the process by which these materials are fabricated, and the clinical outcome of the restoration is determined by the restorative material.

- Ceramic-, metal-, and resin-based crowns and bridges
- Copings and frameworks for metal-ceramic prostheses
- Full and partial dentures
- Inlays, onlays, partial crowns, and provisionals
- Implant abutments and crowns, including screw-retained crowns
- Orthodontic printed models and clear appliances
- Maryland bridges and veneers

Subtractive Manufacturing—CAM Milling Machines

CAD-CAM crown fabrication was the first **subtractive manufacturing** introduced to dentistry in late 1980s. With CAD-CAM technology in a dental office, a patient may receive a crown with the

same-day delivery and reduced chairside adjustments. Representative CAD-CAM systems are offered by Dentsply Sirona (CEREC) and Planmeca USA (Emerald). This group of equipment can be used to fabricate ceramic and composite inlays, onlays, crowns, and veneers from an optical impression of the prepared tooth made from a digital impression. The restoration is designed using the system's software and milled from a solid block of ceramic or composite using diamond and carbide burs. Restorations and prostheses may be prepared in a single appointment, which eliminates the impression material, preparation of a model, preparation of a provisional restoration, and laboratory fabrication of the final restoration or prosthesis.

CAD-CAM Systems

Today's dental CAD-CAM systems can be divided into four groups. The first group is the chairside systems, such as CEREC from Dentsply Sirona and Emerald from Planmeca USA. The Primescan (Dentsply Sirona) uses blue light-emitting diode (LED) light and smart pixel sensor video imaging for 24 frames per second and processes more than 1 million 3-D data points per second. The Emerald uses a multicolor laser-based system.

The second group is the commercial laboratory systems. For these systems, the dentist should send physical impressions, master models, or raw scans to the laboratory of choice for the fabrication of the final prosthesis.

The chairside system usually operates on a closed-architecture format, which requires the scan to be used only within the manufacturer's proprietary CAD-CAM workflow, and this system uses its own specific file format for CAD-CAM functions. The laboratory system uses an open-architecture format that allows a variety of file formats, such as STL, OBJ, and PLY. The STL is the most popular file format in the field. The scan data can be easily exported as an STL file format compared with other file formats.

The third group is stand-alone digital impression systems. This type of system is based on an open-architecture format and takes only intra- or extraoral scans. The raw file format is electronically transferred to a designated commercial laboratory for the fabrication of the final prosthesis. The Medit i500 (Medit Corp) works based on 3-D video technology. The TRIOS 3 (3Shape) uses fast confocal microscopy optical scanning technology. The iTero (Align Technology) uses laser light beams based on parallel confocal microscope technology. The True Definition Scanner (Midmark) uses structured pulsating blue light with active wavefront sampling 3-D video technology. The CS 3600 (Carestream Dental) uses LED light with active-speed 3-D video technology.

The fourth group is hybrid systems; these are a kind of mix-and-match system based on an open-architecture format. A hybrid system allows communication between products of many different manufacturers, such as intra- and extraoral scanners, CAD units, and CAM units. The dentist and laboratory can choose their preferred scanners, CAD-CAM software, computer hardware, 3-D printers, and milling machines from a variety of vendors.

The common disadvantages of the laboratory, digital impression, and hybrid systems are the need for multiple clinical appointments, the making of physical impressions, the fabrication of provisionals, the increased total costs of fabrication, and the delayed delivery time compared with the chairside systems.

CAD-CAM Materials

All classes of dental materials, including ceramics, polymers, and metals, can be processed with CAD-CAM systems. In this chapter, ceramics are discussed, which is the most widely used material, among others.

The CAD-CAM ceramics can be categorized into three main groups, mainly by the glass content, and subgroups by the type of material, as follows:

- Aesthetic ceramics with high glass content
Aluminosilicate (feldspathic or synthetic)—This material is a mixture of high-melting glasses, nepheline, and albite, such as the Mark II (VITA North America).
Lucite (40% to 50%) containing glass—The typical material of this group is IPS e.max (Ivoclar Vivadent).
- Structural ceramics with low glass content
Lithia disilicate and zirconia reinforced lithia silicate—This material group includes e.max CAD (Ivoclar Vivadent), Suprinity (VITA North America), and Celtra Duo (Dentsply Sirona).
Alumina, spinel, and alumina/zirconia—This material group comprises In-Ceram Alumina, In-Ceram Spinel, and In-Ceram Zirconia (VITA North America).
- Structural ceramics without glass content
Polycrystalline alumina (with 3 wt% Mg for grain growth control)—This material group includes VITA All-Cubes (VITA North America).
Polycrystalline zirconia (with 3 to 5 wt% of Y for transformation toughening)—This material group includes VITA YZ HT (VITA North America), CEREC Zirconia Blocks (Dentsply Sirona), IPS e.max ZirCAD LT (Ivoclar Vivadent), and KATANA Zirconia Blocks (Kuraray America).

All materials presented here can be processed by either a chairside or a laboratory milling machine. The commercial labs use disks for bulk production of multiple units, and chairside milling units work with individual blocks. The manufacturers produce only feldspathic (aluminosilicate) blocks for chairside milling. Thus there are no laboratory-milled feldspathic CAD-CAM prostheses.

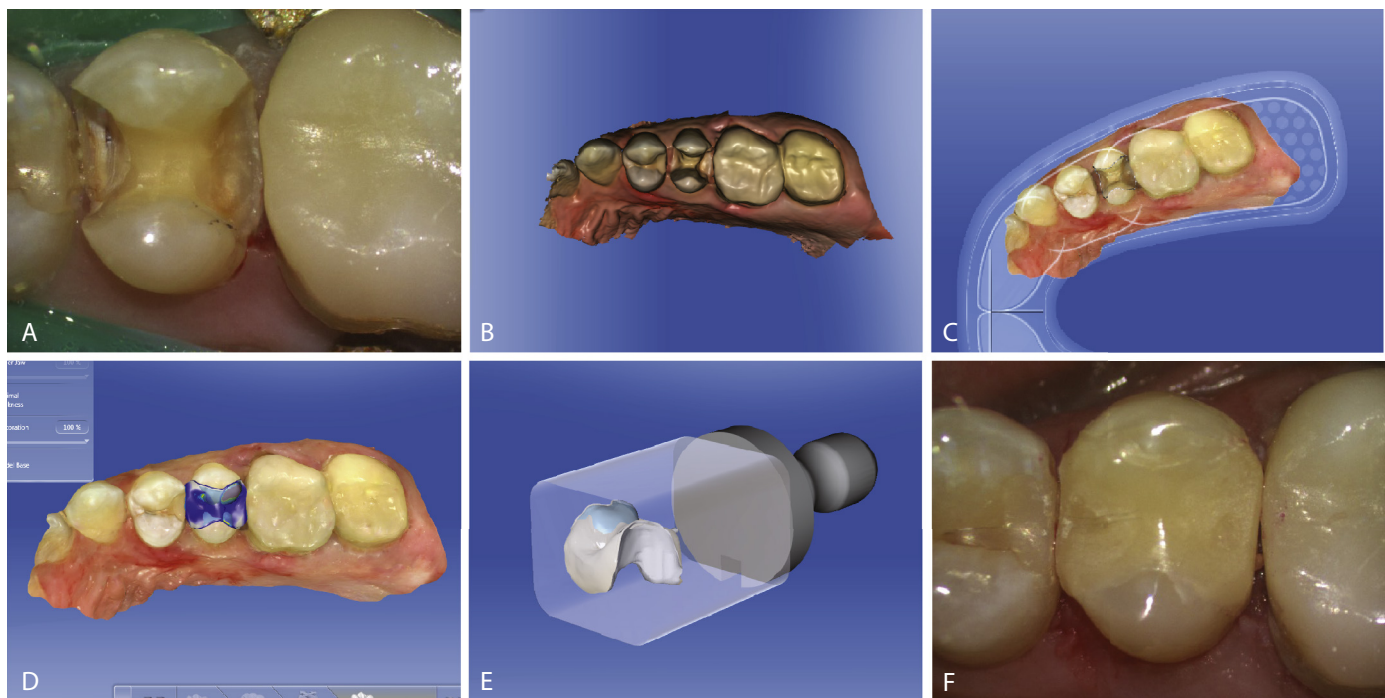
CAD-CAM Case

The advantage of the chairside CAD-CAM systems is that the dentist can create any preparation design to preserve tooth structure as long as enough enamel structure remains for desirable adhesion between the ceramic and the enamel. Because one-visit CAD-CAM dentistry does not require provisional restorations and temporary cement, contamination of the prepared tooth structure is minimized, and the dentist can gain strong bonding for optimal results.

The following clinical case demonstrates a CAD-CAM chairside partial-coverage (inlay or onlay) crown. The occlusal surface of an existing resin composite restoration shows the existence of a large marginal gap but without radiographic evidence of recurrent caries. After the old resin composite restoration was removed, lesions of recurrent caries were revealed. The tooth was prepared to receive a ceramic onlay. Once the cavity preparation was completed (Figure 15-1, A), the intraoral scans of the prepared tooth were made (Figure 15-1, B). Scans of the unprepared teeth of the opposing arch and the buccal bite registration were also taken (not shown). The next step includes the occlusal relation adjustment (Figure 15-1, C) and the design of the prosthesis (Figure 15-1, D). The final preview of the milling process prior to the actual manufacturing process is shown in Figure 15-1, E. The CAD-CAM restorations were then tried and inserted with dual-cure resin cement. The final occlusal photo (Figure 15-1, F) shows a well-integrated aesthetic ceramic restoration.

Additive Manufacturing—3-D Printing

Additive manufacturing (AM) or 3-D printing includes processes in which material is incrementally joined or solidified under computer control to create an object. The object is formed layer by layer, such as fusing of particles or curing of light-sensitive



• **Figure 15-1** Computer-aided design/computer-aided manufacturing (CAD-CAM) processing of an onlay. **A**, Tooth preparation. **B**, Intraoral scan of the preparation. **C**, Occlusal relation adjustment step. **D**, Virtual restoration editing step. **E**, Final milling preview. **F**, Postoperative photo.

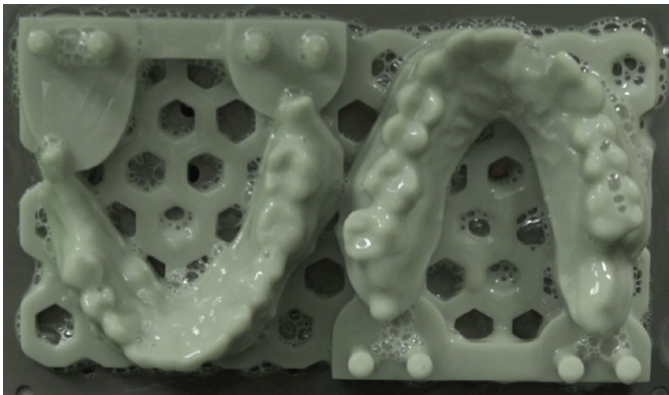
polymers. A key advantage of 3-D printing is the ability to produce very complex geometries of restorations designed from intra-oral impressions.

Desktop 3-D printers use dental resins for the fabrication of temporary prosthetics, surgical guides, orthodontic models, retainers, and aligners. Various dental resins for printing applications may be chosen for any of the desired characteristics, such as transparency for optical clarity, translucency for esthetics, flexibility for patient comfort, or high-impact resins that resist wear and fracture. The most common applications are transparent aligners and night guards. Aligners serve as alternatives to braces and have become especially popular because of their invisibility. This technology may also be used for printing diagnostic casts (Figure 15-2). Oral surgery guides from 3-D printing offer the required precision to verify proper implant positioning where bone is present (Figure 15-3, A), adequate bone reduction for

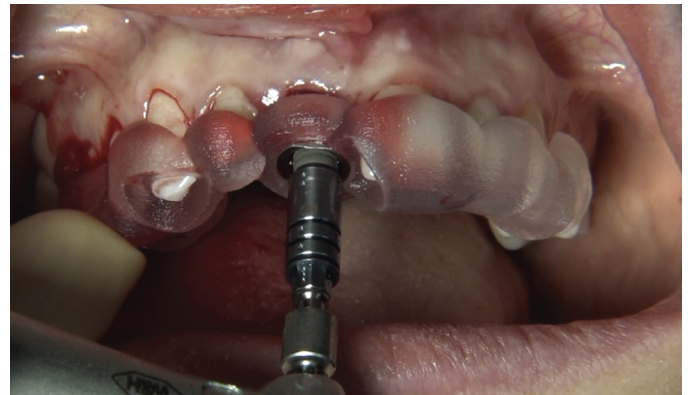
bone recontouring (Figure 15-3, B), and precise drill positions (Figure 15-3, C), to name a few. These guides also facilitate immediate placement and loading of implants where a provisional restoration can be printed prior to the surgery (Figures 15-4 and 15-5). A printable material with contact bactericidal activity is also possible, which may lead to crowns, retainers, aligners, and implants that are resilient to degradation under oral conditions, with longer clinical lifetimes.

Current Additive Manufacturing Technologies

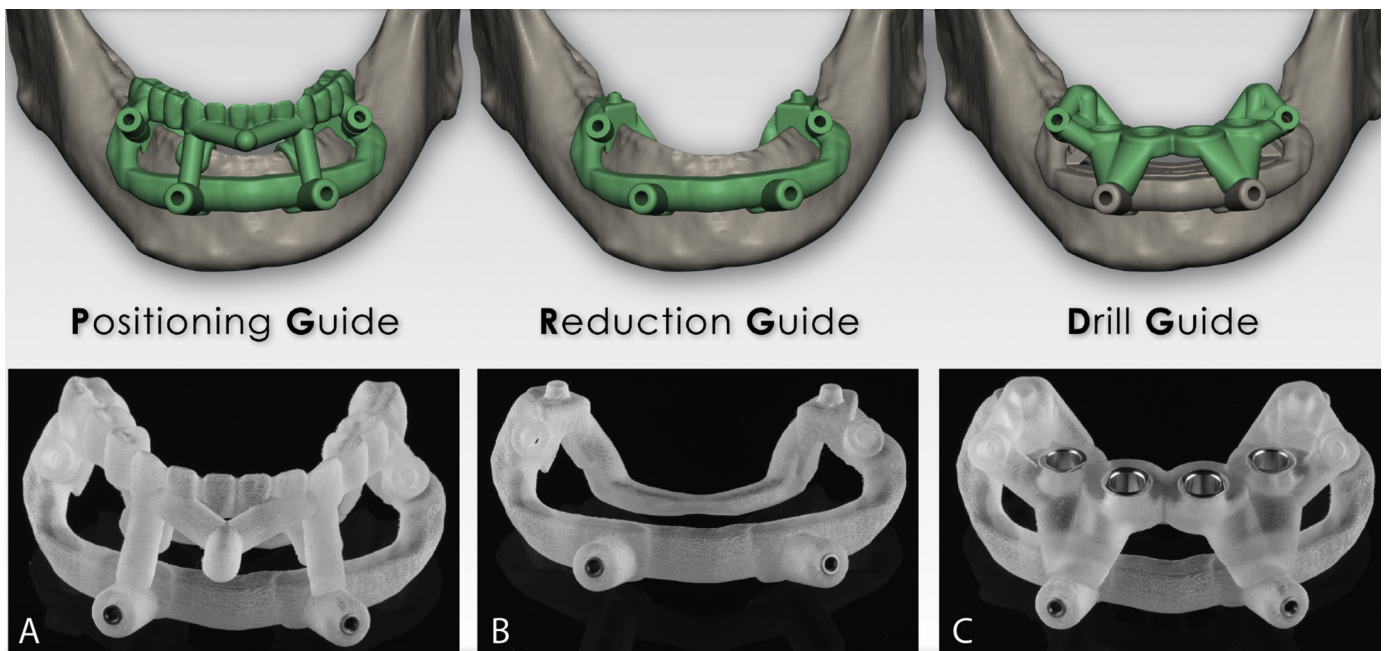
Currently, 3D printing includes stereolithography (SLA), **fused deposition modeling (FDM)**, selective laser melting (SLM), and direct metal laser sintering (DMLS). The most commonly used 3-D printing process (46% as of 2018) is FDM, a material extrusion technique. All 3-D printing requires a CAD file for execution of the manufacturing.



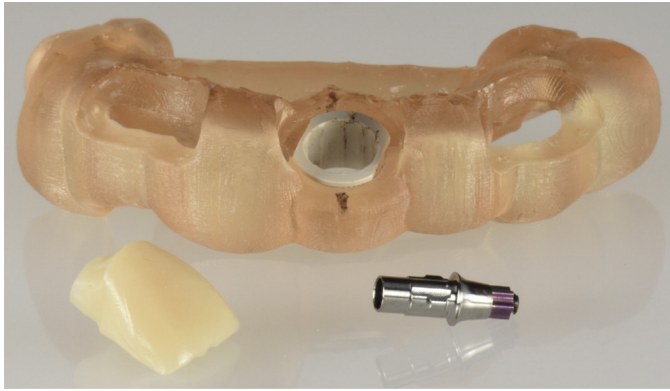
• **Figure 15-2** Three-dimensional (3-D) printed model of diagnostic casts. (Courtesy Dr. Luiz Gonzaga.)



• **Figure 15-4** Surgical placement of anterior implant using a three-dimensional (3-D) surgical guide. (Courtesy Dr. Luiz Gonzaga.)



• **Figure 15-3** A, Computer-aided design/computer-aided manufacturing (CAD-CAM) image of a positioning guide for implant placement (*top*), final processed three-dimensional (3-D) printed guide (*bottom*). B, CAD-CAM image of bone reduction guide (*top*), final 3-D printed guide (*bottom*). C, CAD-CAM image of drill positioning guide (*top*), final 3-D printed guide (*bottom*). (Courtesy Dr. Luiz Gonzaga.)



• **Figure 15-5** Because of the accuracy of this technology, a provisional restoration can be printed to fit exactly where the implant was placed and be loaded immediately. (Courtesy Dr. Luiz Gonzaga.)

Stereolithography

For this CAM method, thin layers of a photo-curable resin are cured to create the computer-designed geometry. Liquid resin is photopolymerized by using small-spot-size LEDs or laser radiation to locally cure the liquid resin. As the liquid resin cures on the surface, the platform holding the object is gradually lowered in the pool of liquid, allowing liquid resin to flow to the area to be cured. The resin objects shown in Figures 15-2 to 15-5 were all made by SLA.

SLA printers achieve the most accurate results because of the precision of the layers this type of printer creates. The thickness of the printed layers can be controlled by adaptive slicing. If the surface has been designed with a high curvature, for example, thinner layers will be applied than would be the case for a low-curvature surface. Adaptive slicing yields a better surface quality than uniform slicing, which minimizes variations in the cusp height across the layers.

Fused Deposition Modeling

This additive technique incrementally deposits molten thermoplastic material according to a CAD file. The item is 3-D printed by layer, and the molten material becomes a solid object as it cools. FDM printing uses an additive-layer approach similar to that in SLA but uses plastic filaments rather than liquid resin. The plastic filament is fed through an extruder that melts and deposits the material layer by layer to form the item.

A filament of thermoplastic, metal wire, or other material is fed into an extrusion nozzle head, which heats the material and controls the extrusion. FDM is restricted in the variation of shapes that may be fabricated. The method is also known also as *fused filament fabrication* (FFF). FDM has been modified to use pellets directly instead of filament. This process is called *fused particle fabrication* (FPF) or *fused granular fabrication* (FGF).

Selective Laser Melting

This AM technique uses a high-power laser to melt and fuse a variety of metal and alloy powders together. The 2-D layers are incrementally melted and assembled to form a 3-D object. SLM is also known as *DMLS* or *laser powder bed fusion* (LPBF). The term *DMLS* is misleading in that the object is melted during production, a variation of liquid-phase sintering.

Materials for Additive Manufacturing

All classes of materials discussed in Chapter 2 are currently used to fabricate objects by AM technology, but these materials need to be in a flowable state or powder for processing. For polymeric objects, photocuring liquid monomers have been used with SLA, and thermoplastic pellets or wires are used with FDM. Postcuring of objects made of SLA is often needed. For metal objects, metal powder form made by atomization is the most popular feedstock that is selectively melted by laser. Even though not all ceramics include or form a liquid phase as with resins and metals, sintering of ceramic particles by selective laser (SLS) is possible. However, these ceramic parts have a rough and porous surface and are suitable as tissue-engineering scaffolds. To improve the densification of ceramic objects, a photocuring liquid filled with a high amount of ceramic fillers is cured with SLA, and the resulting green body is heat-treated in a furnace to burn off resin residue and densify the desired ceramic structure.

The mechanical properties of 3-D printed parts limit the potential of large-scale printing. Therefore an optimized pattern of 3-D printing is important to control flaw sensitivity. Also, changes in the printing environment have an influence on the quality of the finished products. AM is capable of fabricating parts of various sizes, from the micro- to macro-scale. However, the precision of the printed parts is dependent on the accuracy of the method employed and the scale of printing. For instance, micro-scale 3-D printing poses challenges with the resolution, surface finish, and layer bonding, which sometimes require postprocessing techniques such as sintering.

CRITICAL QUESTION

How does CBCT technology differ from quantitative light-induced fluorescence (QLF) and other optical imaging systems?

Diagnostic Systems

Cone-Beam Computed Tomography

CBCT is an imaging technology in which the radiation is divergent and forms a cone. This imaging technology is especially useful for implant dentistry, oral surgery, endodontics, and orthodontics. During imaging, the CBCT x-ray generator and detector rotate around the patient's head. From the digital file, a 3-D rendering is computed that can be used to visualize both erupted and nonerupted teeth, tooth root anatomy, and abnormal structures. Such information is beyond what is possible to see in conventional 2-D radiographs.

CBCT images deliver substantially greater radiation than standard dental 2-D x-ray exams. Thus the enhanced diagnostic sensitivity leads to greater patient radiation exposure. The exposure can be mitigated by

- choosing the scanning protocol in accordance with the minimum diagnostic requirement, or
- using a thyroid collar and leaded glasses when these do not detract from the image quality.

Optically Based Caries Diagnosis

Caries causes demineralization of enamel and dentin. Demineralized areas have greater porosity than the surrounding tissue, which changes the optical properties of the mineral tissue. This change in optical properties is used to locate caries. Quantitative light-induced

fluorescence (QLF) is such a nondestructive diagnostic method for the assessment of early caries lesions. Teeth fluoresce because of the presence of minerals in the enamel and dentin. When a tooth becomes carious, the fluorescence of the carious lesion decreases. The fluorescence image of enamel with incipient lesions can be digitized, and then the loss of fluorescence at the lesion site can be quantified in comparison to the fluorescence of sound enamel. The QLF image provides a measure of the extent and severity of the lesion. Changes in fluorescence and lesion area can be followed over time to measure lesion development before intervention. QLF has been successfully applied to smooth surfaces and occlusal surfaces but not interproximal lesions.

The new QLF-D BiLuminator allows ordinary white-light images to be collected simultaneously with fluorescent images. The images aid in direct visual assessment and highlight features such as leaking restoration margins with secondary caries, occlusal and interproximal caries, sealant integrity, cariogenic activity under sealants, and the presence of calculus and gingivitis. Other recently introduced fluorescent detection systems include the CamX Spectra Caries Detection System (Air Techniques, Melville, NY) and the SoproLIFE Dental Caries Detection System (Acton North America, Mount Laurel, NJ).

CRITICAL QUESTION

How does virtual reality differ from augmented reality?

Virtual and Augmented Reality

Virtual reality (VR) is a computer-generated simulation that allows for interactive experiences and fully re-creates the environment through simulation.

Augmented reality (AR) is considered a form of VR in which interacting with the real world takes place through simulation. The objects and individuals are augmented because they are computer-generated images, but they are perceived in the real world through a camera projected onto a screen.

VR and AR systems have become increasingly common in dental education. Their use has changed clinical training and

encourages self-directed learning. These digital tools are thought to lower the cost of clinical education while increasing the quality.

The Future

As digital dentistry evolves, the incorporation of this technology into dental training and clinical practices will also change. Future dental professionals must be exposed to new digital procedures in the curriculum and teaching.

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16

Materials and Processes for Cutting, Grinding, Finishing, and Polishing

OUTLINE

Benefits of Finishing and Polishing Restorative Materials

Mechanics of Abrasive Procedures

Abrasive Processes in Dentistry

Abrasive Instruments

Finishing and Polishing Procedures

Dentifrices

Summary and Recommendations

Acknowledgment

KEY TERMS

Abrasive A product that has a hard phase as an essential constituent that provides many individual particles with sharp cutting edges.

Air-particle abrasion The process of material removal by way of air-pressure-propelled abrasive particles. Typical applications are surface cleaning, cavity preparation, and surface preparation for bonding. The process is also known as *erosion* in the field of tribology.

Bonded abrasive An abrasive instrument containing a phase that holds abrasive particles in a more or less tight grip with spaces in between that allow air or liquids to pass. The strength of bonding in a product varies based on its intended use. Strong bonding is required for work on hard materials. Breaking away of grains from the bond of an abrasive is desirable as they become dull. Bond materials include organic (resin or rubber), vitrified (glass or glass-ceramic), and metal.

Buffing Polishing with a soft absorbent material such as cloth or leather, typically in combination with a medium containing very fine abrasive particles.

Bulk reduction and contouring An early process that precedes finishing and polishing, whereby excess restorative material is removed to develop the anatomical form of the final restoration.

Cutting Reduction of a material by use of an edged instrument, such as a bladed dental bur, or a bonded abrasive disk or wheel; implies material removal by a slicing action.

Dressing The use of a variety of tools to remove any debris that may be clogging the spaces between abrasive particles on

a bonded abrasive instrument to expose fresh abrasive and restore grinding efficiency. Diamond-coated tools or bonded abrasive stones of aluminum oxide or silicon carbide are the most common devices used for dressing grinding wheels.

Erosion A process of material removal achieved by (1) air-pressure-propelled abrasives (*air-particle abrasion*), (2) pressurized liquid-abrasive mixtures (*slurry erosion*), or (3) chemical dissolution using strong acids or alkali (*chemical erosion* or *acid etching*).

Finishing The process of removing surface defects or scratches created during the contouring process through the use of cutting or grinding instruments or both.

Grinding A machining process that uses coated or bonded abrasive wheels or points to turn against the surface of a material workpiece in order to reduce the surface. Ground surfaces typically display linear scratch marks where abrasive particles have ground material away.

Polish, polishing A process that uses very fine abrasives to bring a material surface to a highly developed, finished, or refined state. A minimal amount of material is removed from the workpiece to generate a smooth, glossy appearance. The force per unit area for polishing is the lightest of all processes that use abrasives.

True/truing A process of correcting the concentricity and shape of a grinding wheel; truing keeps the grinding wheel rotating concentrically with the spindle axis of the motor or handpiece head without vibration or wobble.

As has been stated many times throughout this book, the intraoral surfaces of virtually every direct and indirect restoration must be contoured by various abrasive procedures. The goal of these procedures is to efficiently produce the desired surface contours, contacts, textures, and gloss on a restoration. These procedures involve removing varying

volumes of material from the surface by a process called *wear*. More specifically, they employ abrasive materials and instruments to produce *abrasive wear*. This form of abrasive wear is intentional as opposed to the unintentional type of abrasive wear of composites ([Chapter 5, Wear](#)) and ceramics ([Chapter 10, Abrasiveness to Enamel](#)).

Abrasive processes have been used since prehistoric times. Over 10,000 years ago, hunting and gathering instruments such as spear points, arrowheads, scraper tools, and hoes were formed from hard, rock-like natural materials using primitive forms of abrasion, chipping, grinding, and honing. Sandstone was used to produce smoother surfaces on the Egyptian pyramids. Grinding wheels of a primitive type were created over 4000 years ago by taking a cylindrical stone with an abrasive surface and spinning the stone against metals and ceramics to adjust their shapes, reduce rough areas, and produce smoother surfaces. These processes were refined over subsequent millennia to produce metal daggers, swords, spears, and shields of relatively high quality. The Chinese introduced coated abrasives in the 13th century by embedding seashell fragments in natural gums that were spread on a parchment backing. The invention transformed loose abrasive particles into practical instruments.

In the early 1900s, abrasive technology advanced further through the development and use of alumina grains, diamond particles, and silicon carbide grit. New products in the form of powders, slurries, particle-embedded discs and wheels, and burs of different types emerged for use in dentistry. The further refinement of dental handpieces, air-abrasive technology, and methods of bonding abrasives to various binders led to major processing breakthroughs that have rapidly advanced the quality of treatment in the current era of restorative dentistry, particularly with adhesive and esthetic dentistry. **Figure 16-1** illustrates the series of abrasive procedures and instruments used to bring a rough removable dental prosthesis casting to the final polished state of the prosthesis. The procedures depicted are *sandblasting*, *cutting*, *grinding*, *finishing*, and *polishing*.

The focus of this chapter is to provide the reader with an awareness and broader background of the principles and mechanisms of

tools available to produce optimal surface finish and integrity in dental restorations.

CRITICAL QUESTIONS

What are the benefits of finishing and polishing the surfaces of restorative materials? What are the goals of finishing and polishing?

Benefits of Finishing and Polishing Restorative Materials

Before any dental restoration or appliance is placed permanently in the mouth, it should be polished to a smooth surface. Not only is a rough surface on a restoration, prosthesis, orthodontic appliance, and so forth uncomfortable for the patient, but it can also cause food and other debris to cling to the surface. Such a restoration or appliance becomes unsanitary and, in some cases, tarnished or corroded.

Finished and polished restorations provide four benefits in dental care: patient comfort, better gingival health, chewing efficiency, and esthetics. One study showed that patients could distinguish a difference in roughness from between 0.25 and 0.50 μm by tongue proprioception. The value is much lower than 20 μm as previously reported. Further, surface roughness greater than 1 μm can lead to increased bacterial adhesion and unsightly surface staining. Smooth surfaces resist the accumulation of food debris and permit food to glide freely over occlusal and embrasure surfaces during mastication. Smoother restoration surfaces help patients maintain oral hygiene by facilitating preventive oral home care because dental floss and toothbrush bristles gain better access to all surfaces and marginal areas. Tarnish and corrosion



• **Figure 16-1** Abrasive types used to finish hard metal restorations with complex forms such as Co-Cr alloy partial denture frameworks. **A**, The partial denture framework casting is sandblasted (air-particle abraded) to remove residual casting investment. **B**, A silicon carbide disc is used on a dental lathe to cut the casting sprues. **C**, Mounted corundum stones are used to grind excess metal left from cutting. **D**, A series of rubber bonded abrasives containing progressively smaller silicon carbide grits is used to provide a fine finish to the framework. **E**, Using felts with bar-type abrasives applied to bring the external finish of the framework to a final high-luster polish. (Courtesy Bego USA.)

activity can be significantly reduced on some metallic restorations if their entire surface area is polished ([Chapter 3, Concentration Cell Corrosion](#)).

Rough restoration surfaces, especially those of ceramic-based materials, can abrade and wear opposing dentition and restorations, resulting in the loss of functional and stabilizing contacts between teeth or a reduction in the vertical dimension of occlusion. Rough contact areas on brittle materials can be stress concentration points, leading to chipping and fracture of the restoration. Finishing and polishing of these surfaces will remove surface flaws and improve the restoration's resistance to fracture, especially in areas that are under tension, such as the perimeter of layered all-ceramic crowns where unsupported areas of veneering ceramic are present.

CRITICAL QUESTION

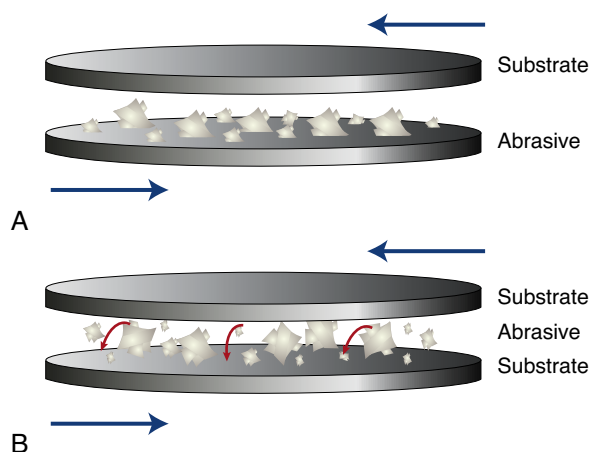
How can the amount of lubricant either increase or decrease cutting efficiency?

Mechanics of Abrasive Procedures

Mechanical abrasion, as described in this section, is a more controlled form of the abrasive wear discussed in [Chapter 4, Wear](#). In dentistry, the abrading instrument is referred to as the *abrasive*, and the restorative material that has been abraded is called the *substrate* or *workpiece*. In this section, we will discuss two mechanisms of abrasive wear used in dentistry: abrasion and erosion. We will also discuss the proper motion of abrasive instruments.

Abrasion

Abrasive wear occurs where a rough, hard object, or a soft surface containing hard particles, slides against a softer surface, digs into the surface, and plows a series of grooves. The material removed during the formation of the grooves, normally in the form of loose particles, is called *wear debris*. A typical example is a diamond bur abrading tooth structure during cavity preparation.

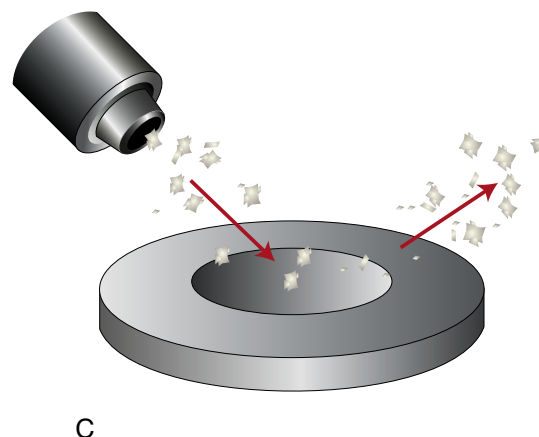


Abrasive wear can also arise in a somewhat different situation when hard abrasive particles are introduced between two sliding surfaces and abrade material from one or both surfaces. The mechanism of this form of abrasive wear seems to be that abrasive particles adhere temporarily to, or become embedded within, one of the sliding surfaces and plow grooves into the opposing surface. An example is the use of nonbonded abrasives such as those in dental prophylaxis pastes. These nonbonded abrasives are placed in a rubber cup, which is rotated against a tooth or material surface.

The two forms of abrasive wear are (1) two-body wear ([Figure 16-2, A](#)), which involves a hard, rough surface; and (2) three-body wear, involving loose, hard abrasive grains ([Figure 16-2, B](#)). These two processes are not mutually exclusive. Diamond particles may debond from a diamond bur and cause three-body wear. Likewise, some abrasive particles in the abrasive paste can become trapped in the surface of a rubber cup and cause two-body wear. Lubricants are often used to minimize the risk of these unintentional shifts from two-body to three-body wear, and vice versa. Thus the efficiency of cutting and grinding will be improved with the use of lubricants such as water, glycerin, or silicone oil. Intraorally, a water-soluble lubricant is preferred. Excessive amounts of lubricant may reduce the cutting efficiency by reducing the contact between the substrate and the abrasive. Too little lubricant results in increased heat generation and reduced cutting efficiency.

Erosion

Erosive wear is caused by hard particles impacting a substrate surface, carried by either a stream of liquid or a stream of air, as occurs in sandblasting a surface ([Figure 16-2, C](#)). Therefore erosion as discussed here is technically a form of abrasive wear that differs only in the mechanism by which the load necessary for wear is delivered. Most dental laboratories have air-driven grit-blasting units that employ hard-particle erosion to remove surface material. A distinction must be made between this type of erosion and chemical erosion. Chemical erosion removes substrate material through the chemical-energy dissolution effects of acids and alkalis versus the mechanical-energy effect



• **Figure 16-2** Illustrations of modes of wear involving abrasive particles. **A**, Two-body abrasion occurs when abrasive particles are tightly bonded to the abrasive instrument that is removing material from the substrate surface. **B**, Three-body abrasion occurs when abrasive particles are free to translate and rotate between two surfaces. **C**, Hard-particle erosion (also called *air-particle abrasion*) is produced when abrasive particles are propelled against a substrate by air pressure.

of force-driven abrasive streams. Chemical erosion, more commonly called *acid etching* in dentistry, is not used as a method of finishing dental materials. This type of erosion is used primarily to prepare tooth surfaces and glass-phase ceramics to enhance bonding or coating.

Abrasive Motion

The motion of abrasive instruments is classified as rotary, planar, or reciprocal. In general, burs act in a rotary motion, flexible discs act in a planar motion, and reciprocating handpieces convert a cyclic motion into a reciprocal direction of motion of the abrasive tool insert. Different abrasive grit sizes can be incorporated with each motion. Reciprocating handpieces provide the special benefit of accessing interproximal and subgingival areas to remove overhangs, finish subgingival margins without creating ditches, and create embrasures.

In the case of a diamond bur abrading a tooth surface, as illustrated in Figure 16-3, *A*, the diamond particles bonded to the bur represent the abrasive, and the tooth is the substrate. Also, note that the bur in the high-speed handpiece rotates in a clockwise direction as observed from the head of the handpiece. The rotational direction of a rotary abrasive instrument is an important factor in controlling the instrument's action on the substrate's surface. When a handpiece and bur are translated in a direction opposite to the rotational direction of the bur at the surface being abraded, a smoother grinding action is achieved (Figure 16-3, *B*). However, when the handpiece and bur are translated in the same direction as the rotational direction of the bur at the surface, the bur tends to "run away" from the surface, thereby producing a less controlled grinding action and a rougher surface. This effect is more noticeable at lower rotational speeds.

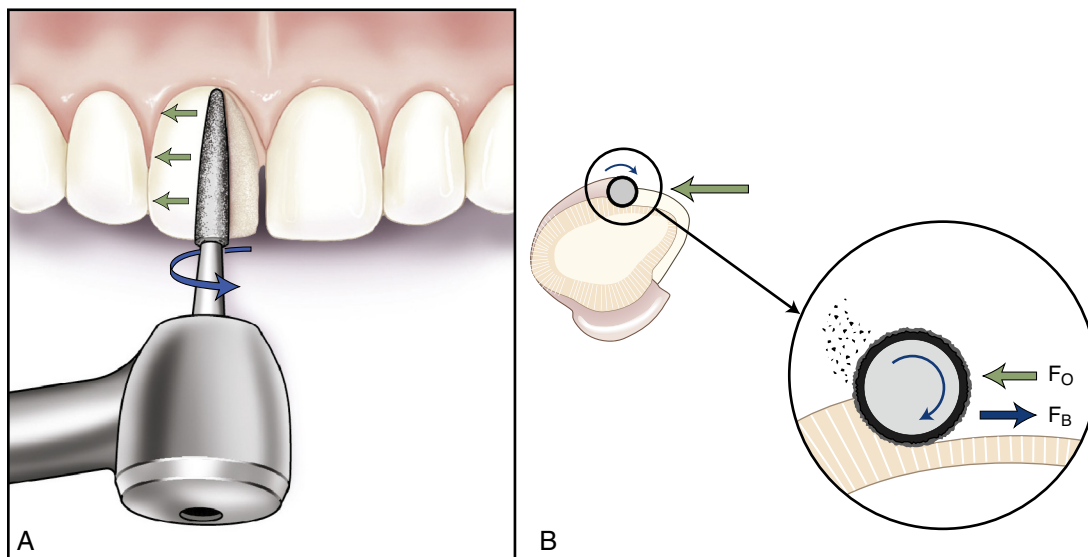
CRITICAL QUESTION

What are the similarities and differences among the mechanisms responsible for the cutting action of carbide burs and abrasive wheels?

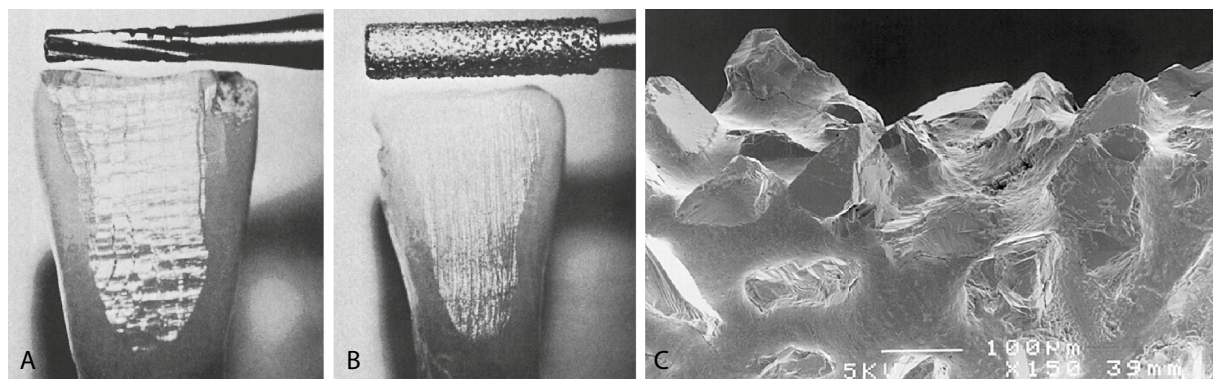
Abrasive Processes in Dentistry

Abrasion is a cutting action, but the topography of an abraded surface is distinctly different from that of a cut surface. In a high-speed tungsten carbide bur, the blades or cutting edges are regularly arranged and allow removal of small pieces or segments of the substrate as the bur rotates. As shown in Figure 16-4, *A*, the pattern of removal of material by the tool corresponds to the regular arrangements of the cutting blades. In contrast with cutting instruments, abrasive tools have many abrasive points that generally are not arranged in an ordered pattern. For example, a diamond rotary instrument may contain hundreds of sharp abrasive points that pass over the workpiece during each revolution of the instrument (Figure 16-4, *B*). Each sharp point acts as an individual blade and removes a chip or shaving from the material. Because these many cutting edges are randomly arranged, innumerable scratches are produced on the surface (Figure 16-4, *C*).

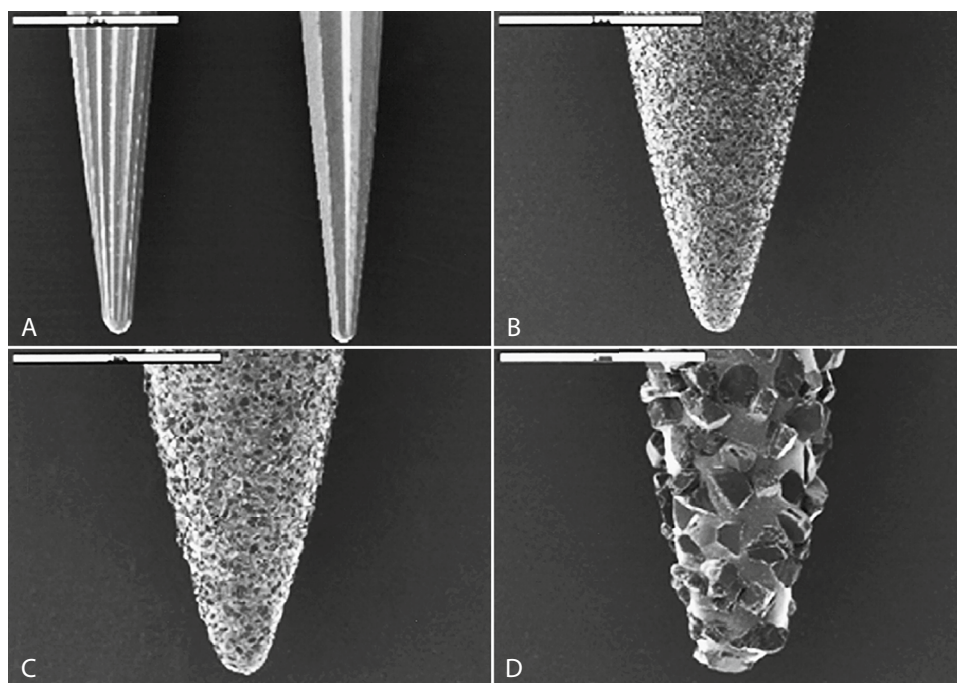
Bulk reduction can be achieved through the use of instruments such as diamond burs, tungsten carbide burs, steel burs, abrasive wheels, and separating discs. Whereas the action of diamond burs and abrasive wheels is often described as grinding, the action of hard blades of steel and carbide burs is described as cutting. Figure 16-5 illustrates two sizes of carbide burs and diamond burs of three grit sizes. Different types of instruments have unique effects on surfaces. A 16-fluted carbide bur produces a smoother finish than an 8-fluted carbide bur, but the latter removes material more rapidly. Similarly, the coarsest diamond bur removes



• **Figure 16-3** The mechanics of high-speed rotary instrumentation. **A**, The blue circular arrow indicates that the high-speed diamond bur rotates in a clockwise direction when viewed from the head of the handpiece. The green arrows indicate the direction that the instrument should be drawn. **B**, Incisal view of the forces generated during high-speed rotary tooth preparation. As the bur rotates in a clockwise direction, it generates a rotational force at the tooth surface, F_B (large blue arrow that represents the reaction force of tooth structure against the rotational force from the bur). The operator of the instrument must generate an opposing force, F_O (green arrow), which should exceed the reaction force to the bur, F_B , and carry the instrument against the tooth surface where the surface will be abraded.



• **Figure 16-4** Bulk reduction of tooth surface. **A**, Tooth cut by a carbide bur. Note the pattern of removal of tooth structure, which corresponds to the arrangement of blades on the bur. **B**, Magnified image of the bonded diamond particles on a coarse diamond bur ($\times 150$). **C**, Tooth ground by a diamond bur. Note the multiple scratches formed by the random arrangement of abrasive particles on the diamond bur.

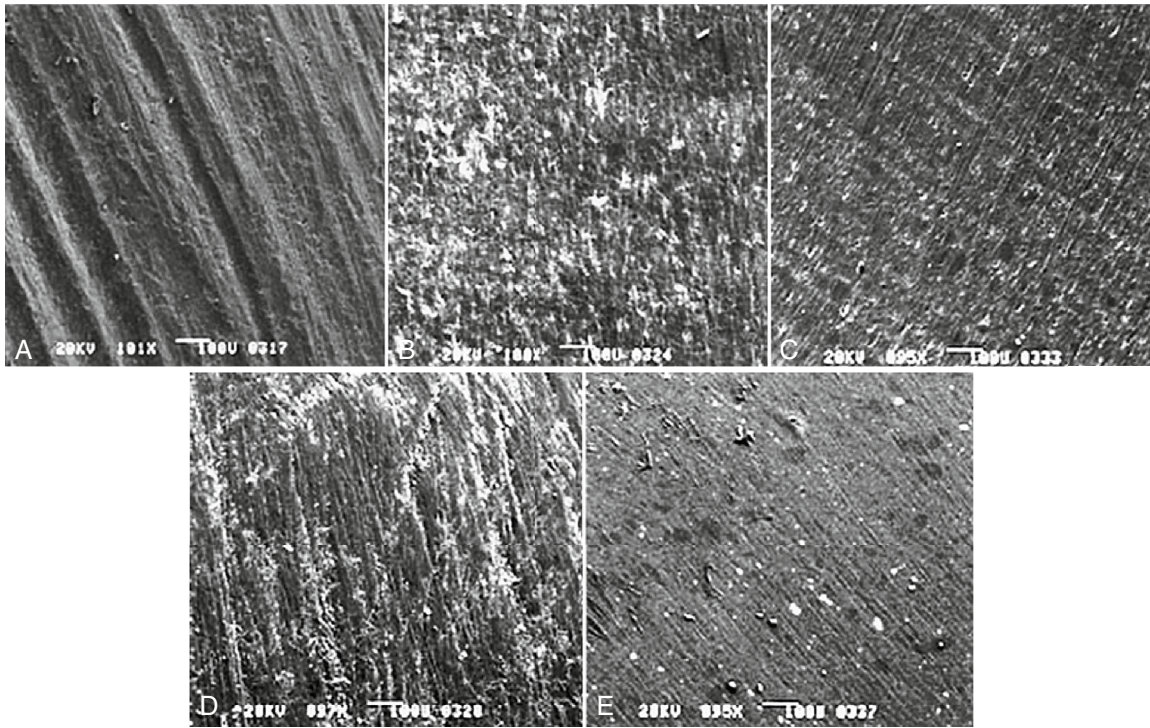


• **Figure 16-5** Instruments for surface reduction. **A**, 16-fluted (*left*) and 8-fluted (*right*) tungsten carbide finishing burs. **B**, Fine diamond bur. **C**, Medium-grit diamond bur. **D**, Coarse-grit diamond bur.

material more quickly but leaves a rougher surface. The scanning electron microscope (SEM) images shown in [Figure 16-6](#) are the surfaces of a resin-based composite produced by five instruments: a coarse diamond, a 12-fluted carbide bur, a 16-fluted carbide bur, an abrasive-coated finishing disc, and an abrasive-coated polishing disc. The first three images represent surfaces of bulk reduction, and the last two represent surfaces of fine finishing.

Rough nodules on a denture base can be removed with an abrasive, such as sandpaper, an emery arbor, or a grinding wheel. In each case, the edges formed by the abrasive particles can remove the rough spots as they move over the surface. Abrasives are available in varying particle sizes. Coarse abrasives leave deep scratches in the surface, which must be removed with finer abrasives. Finally, an abrasive can be so fine that this results in a surface so smooth that the surface reflects light, and the surface is said to be polished.

According to [Figure 16-1](#), after sandblasting, an indirect prosthesis will go through a sequence of four abrasive procedures—cutting, grinding, finishing, and polishing—depending on the type of instruments used, the quantity of material removed from the workpiece, and the purpose. Direct restorations normally do not require cutting. We also use the term *contour* to refer to an abrasive procedure. Dental contouring is a process of removing small amounts of tooth enamel to change the shape, length, or surface of the tooth to improve esthetic appearance or gingival health. The term has evolved to comprise all procedures needed to shape the restoration before finishing and polishing. All four procedures perform abrasive wear, and there are only subtle differences among them. The purpose of the following discussion is not to make a distinction among the four procedures but to present these subtle differences.



• **Figure 16-6** Images of the surface of a resin-based composite after the grinding, finishing, and polishing processes using five instruments: **A**, A coarse diamond. **B**, A 12-flute carbide bur. **C**, A 16-flute carbide bur. **D**, An abrasive-impregnated finishing disc. **E**, An abrasive-impregnated polishing disc.

Cutting

Cutting is generally understood as the removal of a part of a structure by means of a shearing action, as in the removal of diseased tissue with a bladed instrument or any other instrument in a bladelike fashion. Substrates may be divided into separate segments, or they may sustain deep notches and grooves by the cutting operation. Examples of cutting instruments are diamond burs, tungsten carbide burs, steel burs, abrasive wheels, and separating discs. On the other hand, a separating disc is an example of an instrument that can be used in a bladelike fashion. A separating disc does not contain individual blades, but the thin blade design allows the disc to be used in a rotating fashion to grind through cast metal sprues and die-stone materials.

Grinding

A grinding operation is considered to be cutting but on a smaller scale. Small particles of a substrate are removed through the action of bladed or abrasive instruments. Grinding instruments typically contain many randomly arranged abrasive particles. Each particle may contain several sharp points that run along the substrate surface and remove particles of the substrate. Cutting and grinding are both considered predominantly unidirectional in their action. This means that a cut or ground surface exhibits cuts and scratches oriented in one predominant direction.

Finishing

Surface imperfections can be an integral part of the substrate's internal structure or can be created by the instruments used for cutting and grinding. Finishing involves removing marginal irregularities, defining anatomical contours, and smoothing away the surface roughness of a restoration, with the aim of providing a

relatively smooth, blemish-free surface. A good example is the removal of excess material at the junction of the tooth structure and the restorative material to establish a smooth, uniform, and well-adapted cavosurface margin.

CRITICAL QUESTION

How does a clinician know when the smoothest surface has been achieved?

Polishing

Polishing is a special form of abrasive wear characterized by the use of very small abrasive grains (5 μm or less) on an elastic backing. The purpose of polishing is to provide an enamel-like luster to the restoration. Each type of polishing abrasive acts on an extremely thin region of the substrate surface. Polishing progresses from the finest abrasive that can remove scratches from the previous abrasive procedure and is completed when the desired level of surface smoothness is achieved. Polishing should be terminated when no further change in surface luster or glossiness occurs during the application of the finest abrasive that is used for that application. At the end of this process, there should be no visible scratches. However, there will always be scratches appearing at higher magnification. The instrument and the surface must be cleaned between steps because abrasives left from the previous step will continue making scratches. In clinical practice, the quality of the surface finish is usually judged by the surface luster without magnification.

Examples of polishing instruments are rubber abrasive points, fine-particle discs and strips, and fine-particle polishing pastes. Polishing pastes are applied with soft felt points, muslin (woven cotton fabric) wheels, prophylaxis rubber cups, or buffing wheels. Nonabrasive materials, such as felt, leather, rubber, and synthetic

foam, are popular applicator materials for retaining polishing pastes during **buffing** procedures.

Polishing is considered multidirectional, which means that the final surface scratches, albeit invisible, are oriented in many directions. Some examples of ground and polished surfaces are shown in [Figure 16-6](#). Note that the differences in surface appearance are subtle because of the transitional nature of the grinding and polishing processes. If there were larger differences in the size of particles removed, the surface change would be more easily detected.

Heat generation during the abrasive procedures used for direct restorations is a major concern. To avoid adverse effects to the pulp, the clinician must cool the surface with a lubricant, such as an air–water spray, and avoid continuous contact of high-speed rotary instruments with the substrate. Intermittent contact during operation is necessary not only to cool the surface but also to remove debris formed between the substrate and the instrument.

CRITICAL QUESTIONS

What precautions should be taken to minimize the generation of aerosols?
What precautions should be taken to minimize exposure to and inhalation of aerosols?

Biological Hazards of Abrasive Procedures

Dispersions of solid particles are generated and released into the breathing space of laboratories and dental clinics whenever abrasive procedures are performed. These airborne particles may contain tooth structure, dental materials, and microorganisms. Such aerosols have been identified as potential sources of infectious and chronic diseases of the eyes and lungs and present a hazard to dental personnel and their patients. Silicosis, also called *grinder's disease*, is a major illness caused by the inhalation of silica-based aerosols.

The green-state zirconia-based computer-aided design/computer-aided manufacturing (CAD-CAM) blocks for milling prostheses are made from condensed zirconia (3Y-TZP, 4Y-TZP, etc.) particles in the 40- to 90-nm particle-size range. The dust generated from milling is currently classified as an eye, skin, and respiratory irritant. The carcinogenic potential of this material has yet to be determined. The milling generally is conducted in machines equipped with high-efficiency particulate air (HEPA) filtration and is considered safe for the operator. However, technicians and dentists must de-sprue and smooth these prostheses at the workbench prior to the sintering procedure. Therefore, following the protocol of controlling aerosolized dust in the working place is of paramount importance.

Aerosol sources, in both the dental operator and laboratory environments, must be controlled whenever finishing procedures are performed. Aerosols produced during finishing procedures may be controlled in three ways: (1) containing at the source through the use of adequate infection control procedures, water spray, and high-volume suction; (2) using personal protective equipment (PPE) such as safety glasses and disposable face masks that can protect the eyes and respiratory tract from aerosols; and (3) installing an adequate ventilation system that efficiently removes any residual particulates from the air. Many systems are also capable of controlling chemical contaminants such as mercury vapor from amalgam scrap and monomer vapor from acrylic resin.

CRITICAL QUESTION

Why is it sometimes inappropriate to select the hardest abrasive to reduce the time required for finishing and polishing a prosthesis?

Abrasive Instruments

Abrasive particles should be irregular in shape so that they present multiple sharp edges. Most abrasive grits are derived from crushing hard materials and passing particles through a series of mesh screens (sieves) to obtain different particle-size ranges, namely, coarse, medium-coarse, medium, fine, and superfine. [Table 16-1](#) lists grit and particle sizes for commonly used dental abrasives.

An abrasive should be harder than the workpiece the abrasive is supposed to abrade. If the abrasive cannot indent the surface to be abraded, then the abrasive cannot possibly cut the surface. In such a case, the abrasive dulls or wears. The first ranking of the hardness of minerals was published in 1812 by Friedrich Mohs, who ranked 10 minerals by their relative scratch. The least scratch-resistant mineral, talc, received a score of 1, and the most scratch-resistant mineral, diamond, received a score of 10. Despite the lack of precision, a Mohs hardness scale kit can estimate how hard the workpiece is to enable one to select an appropriate instrument to abrade the material with. Knoop and Vickers hardness tests ([Chapter 4, Hardness](#)) quantify the hardness of materials. The farther apart a substrate and an abrasive are in hardness values, the more efficient is the abrasion process. On the basis of a comparison of hardness values for several dental materials listed in [Table 16-2](#), silicon carbide and diamond abrasives are expected to abrade dental porcelain more readily compared with garnet, even though the abrasive particles for all three materials have very sharp edge characteristics.

The inherent strength of cutting blades or abrasive particles on an abrasive instrument must be great enough to remove particles of substrate material without becoming dull or fracturing too rapidly. For example, when a grinding wheel is applied against a metal, the abrasive particle strikes the workpiece suddenly as the metal moves along the circumference of the wheel ([Figure 16-3](#)). If the wheel shatters the instant the wheel contacts the work, the blade is ineffective. On the other hand, if the wheel never fractures, the edge of the wheel may become dull, and the efficiency of the abrasive is reduced. Ideally, the abrasive should fracture rather than dull so that a sharp edge is always present. Fracture of the abrasive is also helpful in shedding the debris accumulated from the work. Although diamond burs cut almost any type of tooth structure or restorative material, the diamond particles do not fracture; rather, they lose substance at the tip. Furthermore, they are likely to become clogged when ductile or soft substances are abraded. They are most effective when used on the very hard and brittle tooth enamel.

The main function of the abrasive is to remove material, yet the final surface finish decides the effectiveness of the abrasives. If too hard of an abrasive is used or if the grain size is too coarse for use on a given material, deep scratches emerge in the substrate that cannot be removed easily in subsequent finishing operations. Additionally, if an abrasive does not have the proper particle shape or does not break down in a manner that creates or exposes new sharp-edged particles, the abrasive will tend to gouge the substrate. A note of caution is warranted here. Subsurface grinding damage, characterized by undetectable flaws or cracks that result from heavy-handed grinding and heat generation, can lead to early, unexplained catastrophic failures in the newer all-ceramic restorative materials such as zirconia, lithia silicate, and lithia disilicate.

As discussed, in order for abrasive particles to remove material from the surface of the dental restoration, they must be harder than the restorative material. Further, the abrasives have to be held against that material with sufficient force to allow the abrasive to

TABLE 16-1 Abrasive Particle Sizes*

Grit/Mesh (USA)	Aluminum Oxide, Silicon Carbide, and Garnet (μm)	Grade [†]	Coated Disc Diamond (μm)	Abrasive Descriptions for Diamond Burs and Diamond Polishing Paste
120	142	Coarse	142	Supercoarse–coarse
150	122		122	Coarse–regular
180	70–86		86	Coarse–regular
240	54–63		60	Fine
320	29–32	Medium	52	Fine
400	20–23		40	Fine–superfine–coarse finishing
600	12–17	Fine	14	Superfine–medium finishing
800	9–12		8	Ultrafine–fine finishing
1200	2–5	Superfine	6	Milling pastes
1500	1–2		4	Polishing pastes (2–5 μm)
2000	1		2	Polishing pastes (2–5 μm)

*Average particle sizes. Grades vary among manufacturers.

[†]Four grades used for a popular brand of aluminum oxide–coated discs. Silicon carbide (SiC) and garnet may vary among manufacturers.

TABLE 16-2 Hardness Values of Abrasives, Tooth Structure, and Dental Materials

Material	Mohs Hardness	Knoop Hardness (kg/mm^2)	Vickers Hardness (kg/mm^2)
Abrasives			
Talc	1	–	–
Gypsum	2	–	12
Tripoli	6	–	–
Pumice	6–7	460–560	–
Porcelain	6–7	560	430
Tin oxide	6–7	–	–
Sand	7	–	–
Cuttle	7	800	–
Quartz	7	820	–
Zirconium oxide (Y-TZP)	7	–	1200–1300
Zirconium silicate	7.5	–	–
Garnet	8–9	1350	–
Emery	7–9	2000	–
Corundum	9	2000	–
Aluminum oxide	9	2100	1200
Tungsten carbide	9.8	1900	–
Silicon carbide	9–10	2500	–
Diamond	10	7000–10,000	–
Tooth			
Cementum	–	40	–
Dentin	3–4	70	62–70
Enamel (apatite)	5	340–431	294–408

Continued

TABLE 16-2 Hardness Values of Abrasives, Tooth Structure, and Dental Materials—Cont'd

Material	Mohs Hardness	Knoop Hardness (kg/mm ²)	Vickers Hardness (kg/mm ²)
Restorative Materials			
Denture base resin	2–3	20	–
Calcite	3	135	–
Metal-reinforced glass ionomer		14–24	40
Type III gold alloy	3	–	122–180 (soft)/155–250 (hard)
Type IV gold alloy	4	220	150–194 (soft)/248–280 (hard)
Amalgam	4–5	90	120 (Ag ₂ Hg ₃ phase)
Rouge	5–6	–	–
Glass (glass–ceramics)	5–6	360	420
Composite (compomer)	–	–	52
Composite (nanohybrid)	–	–	60–62
Composite (nanofilled)	5–7	50–60	73–76
Composite (minifilled)	5–7	50–60	80
Composite (laboratory cured)	–	–	86–124
Titanium	–	–	210
Ti-6Al-4V	–	–	320
Nickel–chromium alloy (as cast)	–	153–328	200–395
Cobalt–chromium alloy (as cast)	–	–	280–380
Layered gold metal–ceramic alloy	–	–	35
Lithia–disilicate (milled)	–	–	550 (milled), 591 (sintered)
Lithia–disilicate (pressed)	–	–	601
Zirconia–reinforced lithia silicate	–	–	~700
Zirconia oxide (Y-TZP)	–	–	1200–1300

penetrate and abrade material from the surface being worked. For any given restorative material, choosing a sufficiently hard abrasive that is strongly bound to the instrument supporting or carrying the abrasive is important so that the abrasive can do the work efficiently. In this section, we will discuss the types of abrasives used in dentistry and how these abrasives are transformed into practical instruments.

Types of Abrasives

Many types of natural and synthetic abrasives are available (Table 16-2), but only those commonly used in dentistry are discussed in this section. Generally, synthetic abrasives are preferred because of their more predictable physical properties.

Aluminum Oxide. Synthetic aluminum oxide (alumina) is somewhat harder than corundum (natural alumina) because of alumina's purity. Several grain sizes of alumina are available and widely used to make **bonded abrasives**, coated abrasives,

and air-propelled grit abrasives. Sintered aluminum oxide is used to make white stones. Pink and ruby variations of aluminum oxide are sold in a vitreous-bonded form as noncontaminating mounted stones for the preparation of metal–ceramic alloy surfaces to receive porcelain.

Arkansas Stone. This material contains microcrystalline quartz and is dense, hard, and uniformly textured. Small pieces of this mineral are attached to metal shanks and trued to various shapes for fine grinding of tooth enamel and metal alloys.

Chalk. A white abrasive composed of calcium carbonate. Chalk is used as a mild abrasive paste to polish tooth enamel, amalgam, and plastic materials.

Cuttle. A white calcareous powder made from the pulverized internal shell of a Mediterranean marine mollusk. Cuttle is available as a coated abrasive and is useful for delicate abrasion operations, such as polishing metal margins and dental amalgam restorations.

Corundum. This is a white mineral form of aluminum oxide. Corundum is most commonly used in an instrument known as a *white stone*. Corundum has largely been replaced by synthetic alpha aluminum oxide in dental applications.

CRITICAL QUESTION

What are the advantages and disadvantages of natural diamond abrasives compared with synthetic diamond abrasives?

Diamond. Diamond is a transparent, colorless mineral composed of carbon atoms in a specific crystalline structure. This is the hardest known substance. Diamond abrasives are supplied in several forms, including bonded abrasive rotary instruments, flexible metal-backed abrasive strips, and diamond polishing pastes.

The advantages of synthetic diamonds over natural diamonds include their consistent size and shape and their lower cost. Synthetic diamond is used in the manufacture of diamond saws, wheels, and burs. Blocks with embedded diamond particles are used to true other types of bonded abrasives. Diamond polishing pastes are also produced from particles smaller than 5 μm in diameter. Synthetic diamond abrasives are used primarily on tooth structure, ceramic materials, and resin-based composite materials.

Emery. This abrasive is a grayish-black corundum prepared in a fine-grain form. Emery is used predominantly in coated abrasive discs and is available in a variety of grit sizes. Emery may also be used for finishing metal alloys or acrylic resin materials.

Garnet. The garnet minerals are the silicates of aluminum, cobalt, iron, magnesium, and manganese. Garnet is extremely hard and, when fractured during the grinding operation, garnet forms sharp, chisel-shaped plates, making this material a highly effective abrasive. Garnet is available on coated discs and arbor bands and is used in grinding metal alloys and acrylic resin materials.

Kieselguhr. This material is composed of the siliceous remains of minute aquatic plants known as *diatoms*. The coarser form of kieselguhr is called *diatomaceous earth* and is used as a filler in many dental materials, such as the hydrocolloid impression materials. Kieselguhr is a mild abrasive.

Pumice. Volcanic activity produces this light-gray highly siliceous material. Pumice is used mainly in grit form but can be found in some rubber-bonded abrasives. Both pumice forms are used on denture bases and in polishing tooth enamel, dental amalgam, and acrylic resins.

Quartz. This is the most commonly used form of silica and is a very hard, colorless, and transparent mineral. It is pulverized to form sharp, angular particles to make coated abrasive discs that are used primarily for finishing metal alloys and grinding dental enamel.

Rouge. Iron oxide is the fine red abrasive component of rouge. Like tripoli, rouge is blended with various soft binders into a cake form. Rouge is used to polish high-noble-metal alloys such as yellow gold alloys.

Sand. Sand is a mixture of small mineral particles predominantly composed of silica. The mixtures are applied under air pressure, through a process called *sandblasting*, to remove refractory investment materials from base-metal alloy castings. They are also coated onto paper discs for grinding metal alloys and acrylic resin materials.

Silicon Carbide. The particles are sharp, and they break to form new sharp particles exhibiting highly efficient cutting of materials, such as alloys, ceramics, and acrylic resin materials. Silicon carbide is available as an abrasive in coated discs and as vitreous- and rubber-bonded instruments in green and blue-black form. The green form is often preferred because substrates are more visible against the green color.

Tin Oxide. This extremely fine abrasive material is used extensively as a polishing agent for polishing teeth and metallic restorations in the mouth. It is mixed with water, alcohol, or glycerin to form a mildly abrasive paste.

Tripoli. This abrasive is derived from a lightweight, friable siliceous sedimentary rock. The rock is ground into very fine particles and formed with soft binders into bars of polishing compound for polishing metal alloys and some acrylic resin materials.

Zirconium Oxide. This abrasive is tougher than aluminum oxide and usually used as a mixture with aluminum oxide primarily in elastic or rubberlike finishing and polishing rotary-shaped instruments.

Zirconium Silicate. Zircon or zirconium silicate (ZrSiO_4) is a mineral that is ground to various particle sizes and used to make coated abrasive discs and strips. ZrSiO_4 is frequently used as a component of dental prophylaxis pastes.

Design of Abrasive Instruments

To achieve the goal of holding abrasives against a workpiece with pressure, abrasives are often mixed with another material to fabricate an instrument for practical applications. Abrasive instruments are generally classified as bonded, coated, and nonbonded. Bonded instruments use a binder to hold abrasive particles together and are molded to form tools of desired sizes and shapes (Figure 16-7). Coated instruments are fabricated by securing abrasive particles to a flexible backing material with an adhesive. These instruments are usually supplied as discs and finishing strips (Figure 16-8). Nonbonded abrasives are loose abrasive particles mixed with water, glycerin, or some other medium to produce a paste or slurry or are propelled by the force of air or water pressure against a workpiece (such as sandblasting for buildings). Each class of instrument is discussed in the following subsections.

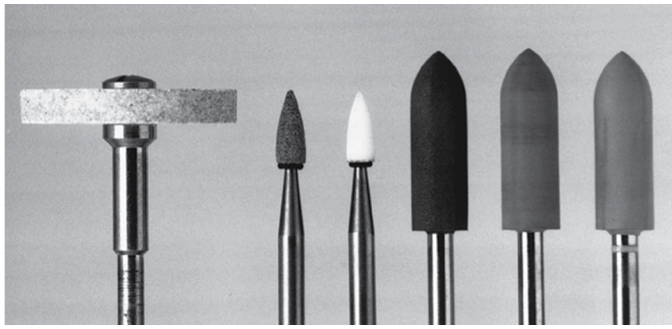
CRITICAL QUESTION

How can one differentiate between high-quality and low-quality bonded abrasive tools?

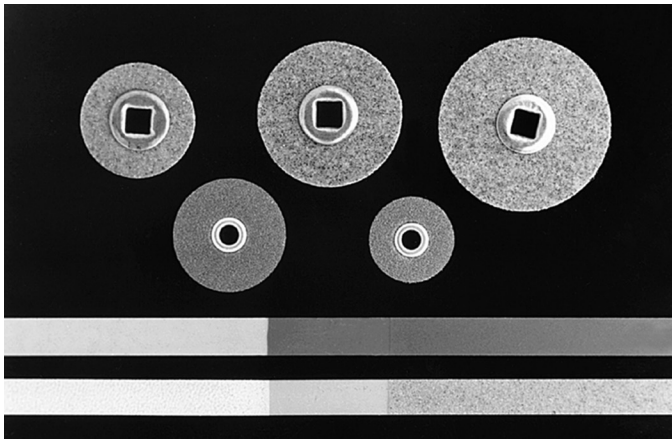
Bonded Abrasives

Bonded abrasives are made by incorporating abrasive particles with a binder to form grinding tools such as points, wheels, separating discs, coated thin discs, and a wide variety of other abrasive instruments. The binder can be organic substances (resinoid, rubber, and so forth), ceramics (glass or glass-ceramic), and metals. Bonding of abrasive particles to the binders can be achieved by sintering, vitrification, and polymerization of binders. Additional methods are also used.

Bonded abrasives that tend to disintegrate rapidly against a substrate are too weak and result in increased abrasive costs because of the reduced instrument life. Those that tend to degrade too slowly get clogged with grinding debris. The result is a loss of



• **Figure 16-7** Typical bonded abrasive instruments used in the dental laboratory include vitreous bonded abrasive wheels and points (*three instruments on left*) and rubber-bonded abrasive bullets (*three instruments on right*).



• **Figure 16-8** Coated abrasive discs and strips. Discs are available in several sizes and with both paper and moisture-resistant backings. Paper-backed discs are represented by the top row of discs; moisture-resistant Mylar-backed discs are shown in the second row. Mylar-backed abrasive strips may be coated with two different grades of abrasive. The coatings are separated in the center of the strip by an uncoated area, which allows the strip to be passed between teeth.

abrasive efficiency, increased heat generation, and increased finishing time. An ideal binder holds the abrasive particles in the tool long enough to cut, grind, or polish the substrate, and yet the binder releases the particles either before cutting efficiency is lost or before heat buildup causes thermal damage to the substrate. Binders are specially formulated for substrate-specific applications.

Sintering is a process of closely packing particles below the melting point of the main components to densify and strengthen a structure by bonding, diffusion, and flow between particles. For example, the head of a bladed tungsten carbide bur is made from a mixture of 5% to 7% of cobalt powder with a balance of tungsten carbide powders and less than 1% of other additives placed under pressure in vacuum and heated to approximately 1350 °C. The sintered head is then welded to a steel shank.

Vitreous-bond materials are composed of finely ground glass-forming materials or ceramic matrix material with which the abrasive is thoroughly mixed. The mixture of binders and abrasive is cold-pressed to the instrument shape and fired to fuse the binder. The vitrified instruments are strong and rigid. They retain high strength at elevated temperatures and are practically unaffected by water, oils, and acids.



• **Figure 16-9** Spiral wheel polishers are designed for maximal flexibility of use on most areas of a restoration. These polishers have a polyamide rubber construction and are available in different diameters with several types and grits of embedded abrasive. Laboratory and clinic polishers are available for use on denture acrylics, composites, ceramics, and precious metals. (Courtesy Dr. Farzan Pouranfar.)

Resinoid-bonded abrasive is a mixture of phenolic resin in powdered or liquid form mixed with the abrasive grains cold-pressed or hot-pressed to a form, then heated to cure. Hot-pressing yields an abrasive binder with extremely low porosity. The reactions are thermosetting processes. Rubber-bonded abrasives are made in a similar manner. Because most of the rubber wheels, cups, and points contain latex, a known allergen, all residues must be removed from polished surfaces. Spiral finishing and abrasive wheels (**Figure 16-9**) are made of synthetic thermoplastic polymers impregnated with aluminum oxide particles.

Metal bonds are used to better retain diamond abrasives to the instrument because diamond is the hardest material known, and diamond grits are expensive and must be used in limited quantities. Metal bonds provide high grit retention and low wear during grinding. Metal bonds are either multilayered by sintering a mixture of metal powder and abrasive particles or single layered by electroplating or brazing. The multilayered method is similar to the sintering process discussed earlier. For the single-layered method, diamond abrasives are bonded to metal wheels and bur blanks with special heat-resistant resins such as polyimides. The supercoarse to fine grades are then electroplated with a refractory metal film such as nickel. **Figure 16-10** shows a set of specialized diamond burs for occlusal reduction of tooth surfaces. The nickel plating provides improved particle retention and acts as a heat sink during grinding. Titanium nitride coatings, seen as a gold color on some diamond abrasive instruments, further extends their longevity.

CRITICAL QUESTION

What are the purposes of truing a grinding instrument?

A bonded abrasive instrument should always be trued and dressed before use. **Truing** is a procedure by which the abrasive instrument is run against a harder abrasive block until the abrasive instrument rotates in the handpiece without eccentricity or run-out when placed on the substrate (**Figure 16-11, A**). The **dressing**

procedure, like truing, is used to shape the instrument, but dressing accomplishes two different purposes as well. First, the dressing procedure reduces the instrument to the correct working size and shape. Second, dressing is used to remove clogged debris from the abrasive instrument to restore grinding efficiency during the finishing operation. The clogging of the abrasive instrument with debris is called *abrasive blinding*. Abrasive blinding occurs when the debris generated from grinding or polishing occludes the small spaces between the abrasive particles on the tool and reduces the depth to which particles can penetrate into the substrate. As a result, abrasive efficiency is lost, and greater heat is generated. A blinded abrasive appears to have a coating of the substrate material

on its surface. Frequent dressing of the abrasive instrument during the finishing operation on a truing instrument, as illustrated in Figure 16-11 (B–E), maintains the efficiency of the abrasive in removing the substrate material.

Diamond instruments are preshaped and trued; they are not treated like other bonded abrasives. Diamond cleaning stones are used on the supercoarse to fine grades to remove debris buildup and to maintain grinding efficiency. An example of a diamond cleaning stone is shown in Figure 16-12. Cleaning stones should not be used on finishing diamonds because their bonded particles are quickly removed. Manufacturers provide special operating and cleaning instructions for these instruments.

Coated Abrasive Discs and Strips

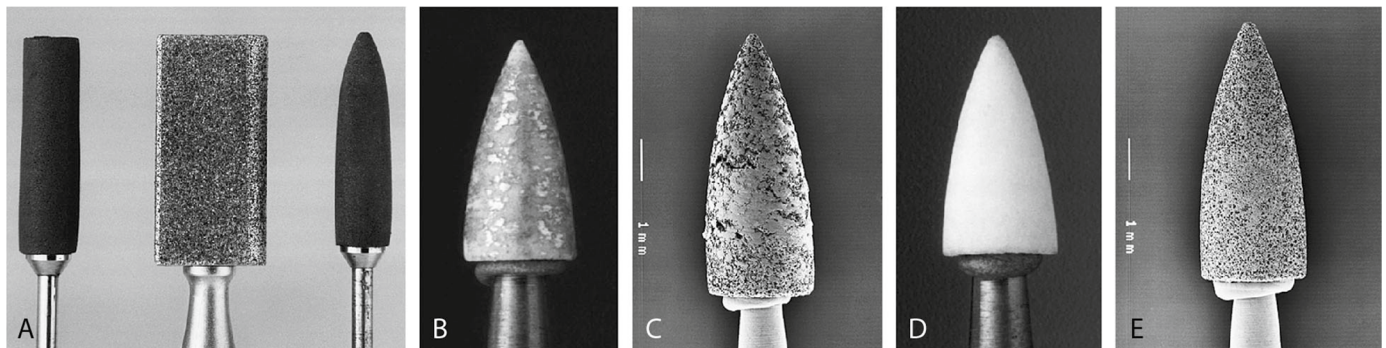
Coated abrasives are fabricated by securing abrasive particles to a flexible backing material (heavyweight paper, metal, or Mylar) with a suitable adhesive material. These abrasives typically are supplied as discs and finishing strips. Discs are available in various diameters and with thin and very thin backing thicknesses. Both metal- and plastic-backed finishing strips are available to smooth and polish the proximal surfaces of all direct and indirect bonded restorations. Metal-backed strips are usually limited to situations in which very tight proximal contacts are involved. Care must be taken to avoid lacerating the gingival tissues. Metal-backed strips are more costly, but they can be autoclaved and used several times if they are not damaged and infection control practice guidelines permit. Plastic-backed strips are used primarily for resin composites, compomers, hybrid ionomers, and resin cements. A further designation is made in regard to whether or not the disc or strip is moisture resistant. The use of abrasive discs or strips with moisture-resistant backings is advantageous because their stiffness is not reduced by water degradation. Furthermore, moisture acts as a lubricant to improve cutting efficiency. Examples of coated abrasives are shown in Figure 16-8.

Nonbonded Abrasives

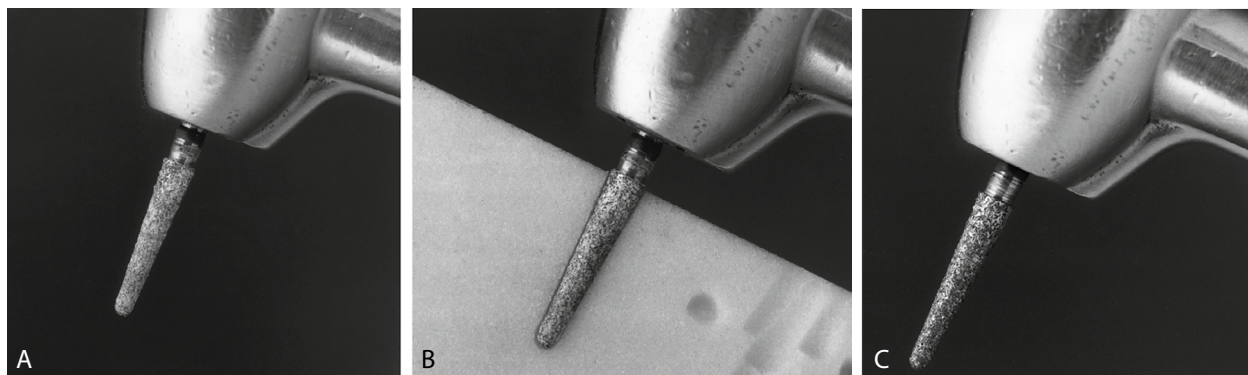
Nonbonded abrasives are primarily used for final finishing and polishing of enamel or restoration surfaces. For example, dental prophylaxis pastes typically contain zirconium silicate. They must



• **Figure 16-10** Specialized diamond burs for occlusal reduction of tooth surfaces. Color-coded bands refer to the depth of occlusal reduction that will be created when grinding to the depth of the wide stop above the diamond-coated portion of the bur. (Courtesy Meisinger USA.)



• **Figure 16-11** A dressing tool is used to true, shape, and clean bonded abrasive instruments both before and during the finishing procedure. **A**, A rubber-bonded abrasive cylinder (left) shows irregular external contours, which will cause it to run eccentrically. The cylinder is first trued against a diamond-coated abrasive dressing tool (center) to make it rotate around the central axis of the instrument. Once trued, the abrasive is further dressed to a desired working shape (right). **B**, Instruments that are blinded with debris lose their cutting efficiency and generate more heat during operation. Note the coating of debris on the abrasive surface. **C**, A scanning electron micrograph of the same instrument reveals the significant amount of debris that is clogging the instrument surface. **D**, Frequent dressing of the abrasive on the dressing tool shown in (A) removes accumulated debris. **E**, A scanning electron micrograph of the blinded abrasive shown in (C) after dressing reveals that the debris has been removed and the abrasive surface restored.



• **Figure 16-12** Removing debris from diamond instruments with a diamond cleaning stone. **A**, Diamond bur in high-speed rotary handpiece before cleaning. Note the accumulated debris. **B**, The bur is cleaned by running it against the moistened diamond cleaning stone for 2 to 4 seconds. **C**, The cleaned diamond bur has no debris remaining among the diamond abrasive particles.

be applied to the substrate with a nonabrasive carrier such as synthetic foam, rubber, felt, or chamois cloth. The abrasive particles are dispersed in a water-soluble medium such as glycerin.

Abrasive pastes used on restorative materials contain either aluminum oxide (alumina) or diamond particles. Alumina pastes should be used with a rotary instrument and increasing amounts of water as the polishing process proceeds from coarser to finer abrasive particles. Diamond abrasive pastes are used in a relatively dry condition. The instruments that apply the paste to the material surface are equally important. These include ribbed proph cups (the ribbed type or the more flexible nonribbed type), brushes, and felt wheels.

Abrasive pastes have several disadvantages: (1) they are relatively thick and cannot gain access to embrasures, (2) the pastes tend to splatter when they spin off the instruments at excessive rotational speeds or if they become wet, and (3) heat is generated when insufficient coolant is used or when continuous polishing pressure is applied without allowing the coolant to reach the surface. More recently, diamond-impregnated spiral polishing instruments such as the Sof-Lex Diamond Polishing System (3M ESPE, St. Paul, MN) have been introduced and offer an alternative to paste abrasives.

Nonbonded abrasives are used for **air-particle abrasion** of restoration surfaces. In dry form, aluminum oxide powders, in 50- to 100- μ m sizes, are used to prepare internal crown and veneer surfaces for cementation and bonding procedures. Desiccated silica glass beads are similarly used to remove investment materials from pressed ceramic castings.

CRITICAL QUESTION

Which procedure will ensure that progressively finer abrasives completely remove scratches made by previous coarse abrasives?

Finishing and Polishing Procedures

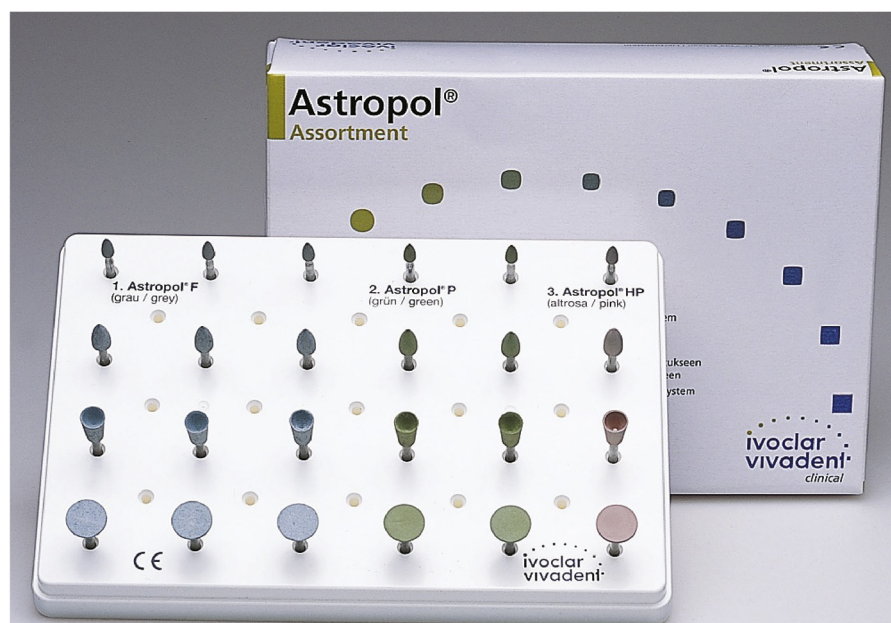
Dental abrasives have many uses in both clinical and laboratory settings. They are used for dental prophylaxis procedures and for the adjustment and preparation of natural tooth structures. They are used extensively for **bulk reduction and contouring**, finishing, and polishing of the wide array of available dental materials. Therefore abrasives are available in a variety of hardnesses and

come in the form of powders; pastes; nickel-plated diamond burs; and bonded abrasive stones, discs, wheels, points, and cups. The best choice for any dental application depends on the substrate material type, the substrate's initial surface quality, and the operator's specific needs. Specific needs vary from cutting or rough grinding to final polishing to achieve a desired luster or gloss.

Almost all direct restorative materials have an initial softer state that can be preshaped to achieve a near-final form prior to hardening; so, again, finer abrasives are generally required to finish and polish direct restorations. An ideal abrasive instrument will perform removal of surface material, and the abrasive binder will release worn abrasive particles to expose newer, sharper ones as the finishing operation proceeds before potentially damaging heat is generated as a result of lack of abrasion from particle loss or the instrument clogging with debris. Hard materials such as metal alloys and ceramics require harder abrasives with strong binders, whereas softer resin-based composites do not. Although flexible abrasive discs designed for contouring and polishing resin-based composites can be used on metal alloys, they are only useful for final polishing because even though their abrasive particles are sufficiently strong, their adhesive binders are weak.

The physical form and stiffness of a polishing instrument also affects the manner of material removal and the surface finish. For example, Sof-Lex and Sof-Lex XT Extra Thin (3M ESPE, St. Paul, MN) contouring and polishing discs for resin-based materials are available in the same four abrasive grades: course, medium, fine, and superfine. Sof-Lex discs have soft, flexible backings, whereas the XT discs have thinner, stiffer backings. Although light or heavy pressure can be applied with either style disc, the softer backing of the Sof-Lex disc allows the disc to flex and adapt more readily to rounded surfaces, especially at lower rotational speeds. The thinner, stiffer XT discs are designed to access tighter spaces without buckling for the development of anatomy like narrow embrasure contours. When placed against rounded contours, XT discs tend to create flat spots because of their stiffness. Both forms yield specific advantages in specific areas of application. These discs are color coded, with darker colors representing coarser grades of abrasives. However, abrasive discs and strips available from other manufacturers may not follow the same coding scheme.

Comprehensive restorative material finishing sets are becoming increasingly popular in that they provide for finishing and polishing of all areas of the restoration. Many come in single-use set packaging for better infection control. For example, the



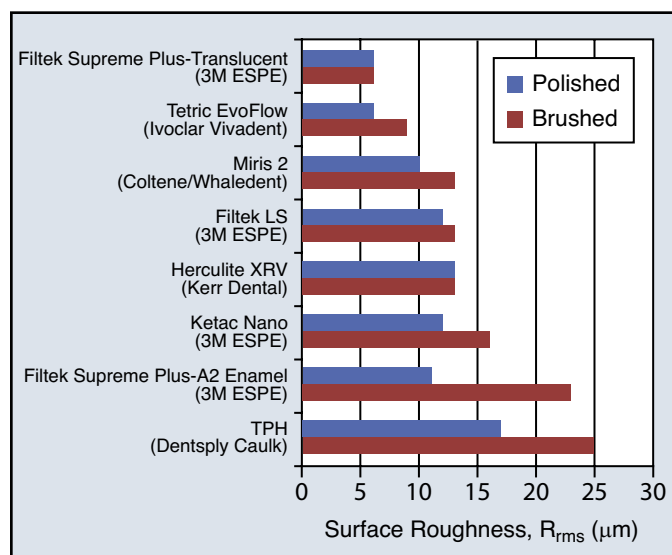
• **Figure 16-13** The Astropol polishing kit comprises four shapes made with three grit sizes—prepolish (blue), polish (green), and high-gloss polish (pink)—and polishers suitable for both resin composite materials and amalgam. (Courtesy Ivoclar Vivadent.)

Astropol finishing and polishing set (Figure 16-13; Ivoclar Vivadent, Amherst, NY) for composites and ceromers comes in four different instrument shapes and three levels of abrasiveness. The four shapes provide for interdental and occlusal applications, and the three abrasive grades, Astropol F, Astropol P, and Astropol HP, allow for prepolishing, polishing, and high-gloss polishing, respectively. Polishing systems are available from dental abrasive instrument manufacturers for each category of dental materials.

The manufacturers also provide information about the abrasive instruments, such as the type of abrasive and binder used, intended applications, recommended speed of the instrument, storage, sterilization, coolant requirement, and block for dressing. The laboratory technician and clinician should familiarize themselves with the instructions for use (IFUs) provided for the instrument selected and recommendations to avoid cross-contamination of instruments used between certain materials.

Resin-Based Composite Restorations

Dental composites are among the most difficult types of materials to predictably finish and polish to a high luster because they contain a relatively soft resin matrix and hard fillers of various sizes in their structures. Figure 16-14 shows the surface roughness values, in root mean squares (R_{rms}), of some resin-based composites when finished with Al_2O_3 discs and then subjected to 20,000 toothbrushing cycles with dentifrices. The differences in values mean that there must be selective grinding associated with the soft resin matrix and the harder particle fillers. In addition, the final finish of a composite restoration depends on the composition, cavity design, curing effectiveness, and postcuring time needed to achieve the restoration's final properties. For some composite materials, delayed finishing is recommended to allow more polymerization to occur. Manufacturers' recommendations often include the thickness of increments and the curing time needed with a light-curing unit of known irradiance in mW/cm^2 .



• **Figure 16-14** Surface roughness (R_{rms}) of various resin-based composites after polishing with Al_2O_3 discs and then subjecting to 20,000 toothbrushing cycles with paste dentifrice at 200 g of weight. (Adapted from Phark J-H et al: Influence of tooth brushing on surface roughness of restorative materials. AADR Abstract #1052, 2010.)

The finishing and polishing technique consists of three essential steps: First, contour the restoration either with 12-fluted carbide burs, 30- to 100- μm diamond burs, or coarse abrasive-coated discs, depending on the dentist's preference. Next, finish with 16- to 30-fluted carbide burs, fine and extra-fine diamond burs, white stones, white Arkansas stones, or medium and fine abrasive-coated discs. Finally, polish with fine and extra-fine polishing paste (alumina or diamond); extra-fine abrasive-coated discs; silicon carbide-impregnated brushes; or diamond-impregnated rubber polishing discs, cups, or points. Most finishing and polishing systems, whether impregnated or coated with abrasive, are available

in a variety of color-coded kits (Figure 16-13). The manufacturers' instructions for their use must be followed to obtain the optimal outcome.

During each stage of finishing and polishing, the operator should proceed in one direction only. Then, after the use of the next abrasive in the sequence, polishing should continue in a direction perpendicular to the previous one. This process ensures that scratches become more visible and that the effectiveness of scratch removal can be assessed more rapidly. The recommended abrasives and polishing instruments should be used in the proper sequence, and intermediate abrasive steps should never be skipped. For example, following a coarse abrasive disc with a fine abrasive rather than a medium-grit abrasive would leave some of the scratches produced by the coarse abrasive. The operator can choose to use one system from start to finish (e.g., abrasive-coated or flexible abrasive-impregnated rubber discs) or combine different systems based on preference and the location of the restoration (e.g., sandpaper for anterior or a brush for posterior sites).

Dental Amalgam

Burnishing prior to carving allows for the removal of the excess mercury and improves marginal adaptation and burnishing after carving improves smoothness. However, burnishing alone will not provide a completely scratch- and retention-free surface for amalgam restorations (Figure 8-12, A). Slow-speed handpieces should be used for finishing and polishing amalgam restorations. In the past, a recommendation was made to wait 24 hours before polishing amalgam restorations to allow amalgam to set completely. However, if the restoration's surface is finished initially with a very fine prophylaxis paste applied with a cotton pellet or a nonribbed rubber prophyl cup rotated at slow speed and light pressure, a smooth, velvety finish is achieved that will acquire a luster as the restoration is abraded normally in the mouth. Spherical amalgams set faster and can be finished and polished sooner.

If amalgam has hardened to an advanced stage in which the abrasion by a fine prophylaxis paste is no longer effective, the following procedure may be used at the next dental appointment: (1) Contour with slow-speed green stones or diamond burs or brown and green rubber points, and (2) apply a mixture of fine pumice and water or alcohol with a rotary brush or felt wheel to polish the surface.

Dental Alloys

Pure gold, a noble metal, is a very soft and ductile metal. Gold is almost never used in the purest form for dental restorations. Recall the discussion in Chapter 2, *Solid-State Reactions in High-Noble and Noble Alloy Systems*, that when alloyed with other metals such as silver and copper, the resultant gold alloy becomes sufficiently hard to withstand masticatory forces without creep or distortion. Many dentists still prefer high-noble alloys because of their workability and adaptability. This quality can be considered a favorable combination of an adequately low yield strength with sufficient percent elongation to allow for the burnishing of restoration margins. Lower-hardness noble-metal alloys require a different finishing approach from that used for the harder, predominantly base-metal alloys used in dentistry. Slow-speed handpieces should be used for finishing and polishing gold and softer noble alloys. This technique consists of the following steps: (1) Contour with fine carbide burs, green stones (silicon carbide) or heatless stones; (2) finish with pink or white stones or medium-grade abrasive-impregnated rubber wheels and

points (brown and green); (3) apply fine abrasive-impregnated rubber wheels, cups, and points; and (4) apply tripoli or rouge with rag or leather wheels, if necessary.

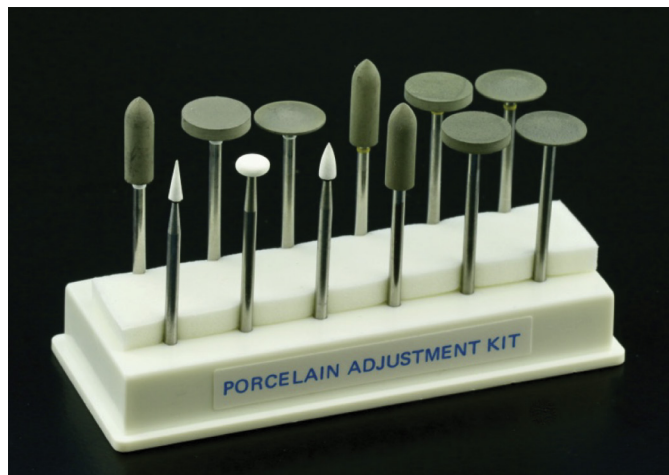
Predominantly base-metal alloys, on the other hand, typically exhibit much higher hardness and yield strengths. They are much harder to finish. Burnishing these alloys is practically impossible. A similar sequence is followed for predominantly base-metal alloys but with more durable abrasive instruments that contain stronger binders. This means that the same carbide burs, stones, and rubber-bonded abrasive instruments will degrade faster when used on the harder alloys. If possible, select instruments with stronger abrasive binders that can withstand the higher abrasive forces generated on these alloys. Fortunately, most manufacturers offer material-specific lines of carbide burs and bonded abrasive wheels and points.

CRITICAL QUESTION

What are the differences between finishing and polishing a ceramic restoration extraorally and intraorally?

Ceramic Restorations

The ideal surface for a ceramic restoration is a polished and glazed one. Esthetic areas are typically contoured and textured first before being polished to a desired level of luster. Proximal and functional contact areas must always be brought to their smoothest state in order to cause the least possible wear under function. Natural glaze (autoglaze) is preferred over the application of glaze ceramic (overglaze). A natural glaze wears less over time because the glaze is a fused surface of the underlying porcelain material as opposed to a coating of weaker add-on glaze ceramic. Natural glazing is not possible for zirconia and lithia disilicate. After polishing is completed, the only glaze option is the application of glaze ceramics on esthetic, nonfunctional areas. Glazing does not necessarily yield a smooth surface if the initial ceramic surface has significant roughness. A desired smooth ceramic surface should be produced through careful extraoral polishing prior to any glazing procedure. Extraoral finishing and polishing instruments (Figure 16-15) come in a wider variety, and access to all areas of the restoration



• **Figure 16-15** Extraoral porcelain finishing kit. Note bands on the mandrels (shanks) to distinguish the levels of abrasiveness. No band indicates a standard prepolymer, yellow indicates a polisher, and white indicates a super-polisher. (Courtesy Dr. Farzan Pouranfar.)

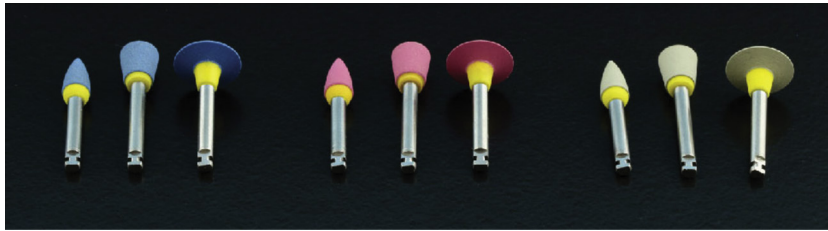
is possible. Intraorally, only minor roughness can be successfully polished with a different set of instruments (**Figure 16-16**) without compromising the surface quality. Frictional heat is detrimental to all ceramic materials, so adequate cooling is necessary whenever ceramic restorations are finished and polished. The use of an air/water spray device and the maintenance of intermittent contact between the restoration and the rotary instrument are critical during any intraoral adjustment operation. Continuous contact between the restoration and the rotary instrument should be avoided.

Manufacturers normally produce material-specific ceramic finishing and polishing kits based on the hardness and composition of the ceramic. **Figure 16-17** shows a typical set of two kits for zirconia-based ceramics. Again, the manufacturers' IFUs should be followed when these systems are used.

Many new CAD-CAM ceramic materials come in a softer, more machinable, presintered state and are intended to be machined then prepolished prior to final sintering. They are designed this way in order to permit grinding with reduced chipping damage to delicate restoration margins, in addition to reducing wear on

milling burs. Depending on the dentist's preference, a general technique is as follows: (1) Contour or mill the ceramic surface with bonded synthetic or natural diamond burs, wheels, and discs; (2) separate milling sprues if necessary, texture, and prefinish with synthetic diamond or aluminum-oxide stones followed by flexible polymer or rubber-bonded fine abrasive wheels, discs, cups, and points (typically a two- or three-step process depending on the material system used); (3) ultrasonically and/or steam-clean polished surfaces thoroughly; (4) apply an overglaze layer or initiate natural glaze on the ceramic if necessary; and (5) final polish with ultrafine abrasive-impregnated rubber discs, cups, and points if necessary. The highest luster may be achieved using a diamond paste applied with a brush or felt wheel. For intraoral adjustments and polishing, use intermittent applications of rotary instruments with copious amount of air/water spray.

Monolithic zirconia, Y-TZP based ceramic materials, is now widely used. This material is incredibly hard to adjust and polish in a fully sintered state; these procedures can be done with instruments specifically designed for zirconia (**Figure 16-18**), but they are time-consuming. For those providing chairside

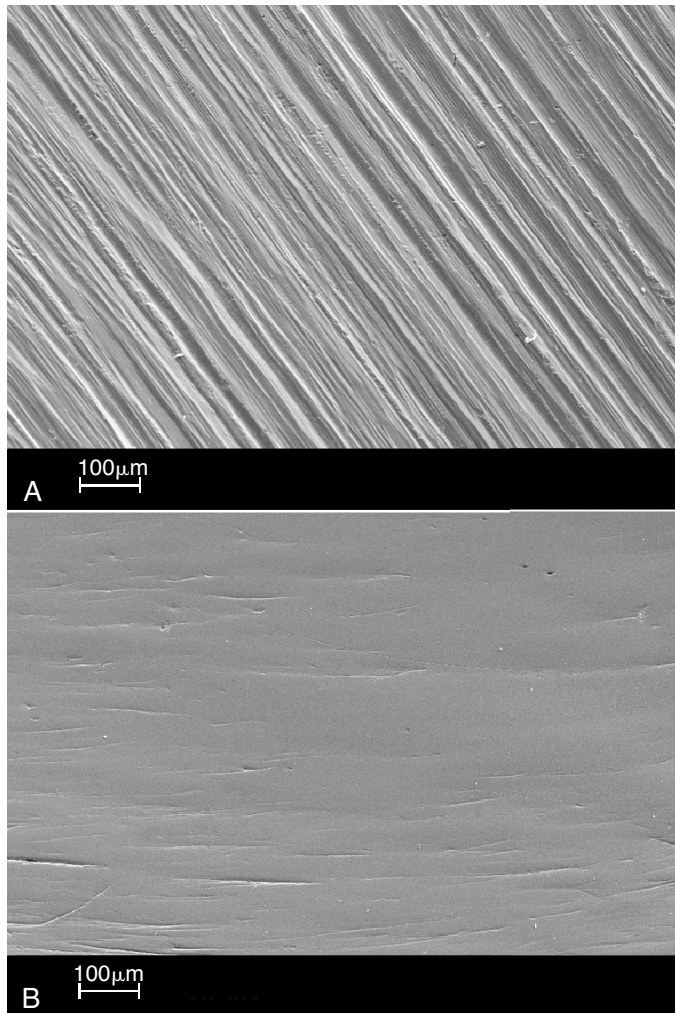


• **Figure 16-16** Intraoral ceramic polishers for laminate veneer (Dialite intraoral polishers; Brasseler USA). Abrasive levels are blue (coarse), pink (medium), and gray (fine). (Courtesy Dr. Farzan Pournafar)



• **Figure 16-17** Typical finishing and polishing kits for zirconia ceramics: extraoral kit for laboratory use (left) and intraoral kit for chairside use (right). Note that the extraoral kits for laboratory kits contain abrasives that will allow for heavier adjustments. (Courtesy Meisinger USA.)

CAD-CAM zirconia restorations, carefully contouring and polishing milled zirconia restorations in their presintered state is recommended so that the sintered restorations have a near-perfect surface upon removal from the sintering furnace. This approach greatly reduces or eliminates the need for



• **Figure 16-18** Effect of instrument on the polished surface. **A**, Zirconia surface finished with a fine diamond bur. **B**, Zirconia surface polished using the Dialite/Diashine system for zirconia. (Courtesy Dr. Siegfward Heintze.)

postsintering finishing and polishing. **Figure 16-19** shows that milling markings will persist after sintering if not removed. In addition to time savings, there are two additional advantages to this approach: avoiding the risk of weakening the restoration from the conversion of the tetragonal zirconia phase to the monoclinic phase caused by grinding (**Chapter 10, Transformation Toughening**) and eliminating the risk of creating a displeasing pearl-like surface appearance to the restoration from polishing.

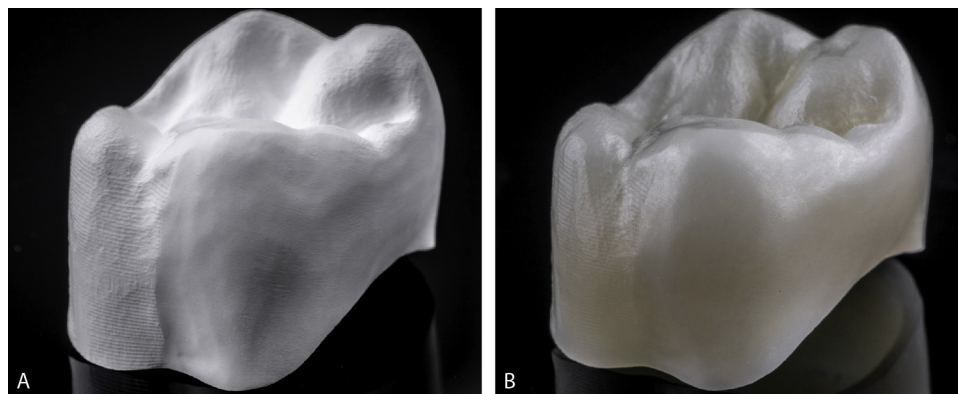
As mentioned previously, leaving rough contact surfaces on zirconia restorations is not recommended. Rough zirconia will cause severe wear of opposing enamel and restorative materials. Glaze ceramic layers over rough zirconia will eventually wear and expose the rough-milled surface of the zirconia (**Figure 16-20**), which can cause greater wear on opposing enamel surfaces (**Figure 16-21**). Lawson and colleagues demonstrated the advantages of placing polished zirconia and lithia disilicate in opposing contact with natural enamel.

Acrylic Resins for Denture Bases and Veneers

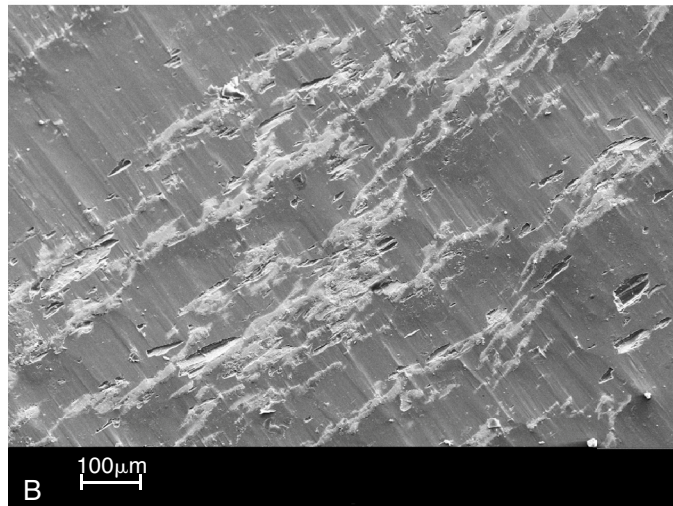
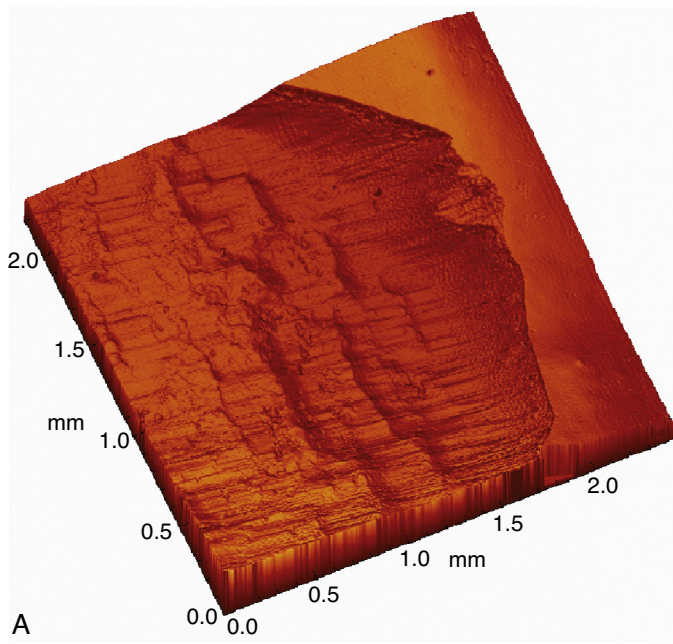
Acrylic resins and other polymers are relatively soft materials. To avoid overheating during finishing, a large amount of pumice slurry should be fed to the work surface as the denture is moved against the rag wheel on the lathe. When using carbide burs and rubber-bonded polishers, intermittent contact with the substrate will help avoid overheating. The following technique is recommended: (1) Contour with tungsten carbide burs and sandpaper abrasive mandrels; (2) use a rubber-bonded abrasive point to remove the scratches; (3) depending on the size of the area that needs to be polished, apply pumice with a rag wheel, felt wheel, bristle brush, or prophyl cup; and (4) apply a mixture of chalk and alcohol or bar-type acrylic polishing compounds with a rag wheel.

Air-Particle Abrasion Technology

As an alternative to the use of rotary instrument cutting, air-particle abrasive systems can deliver a fine, precisely controlled high-pressure stream of 25- to 30-µm abrasive particles to remove enamel, dentin, and restorative materials for cavity preparation. Because air-particle abrasion generates minimal



• **Figure 16-19** Effect of sintering on milled and partially prepolished zirconia crown. **A**, Presintered zirconia crown showing as-milled surface (*left*) and prepolished surface (*right*). **B**, Same restoration after fully sintering. Note difference in smoothness and that sintering does not remove milling striations. (Courtesy Dr. Troy Decker.)

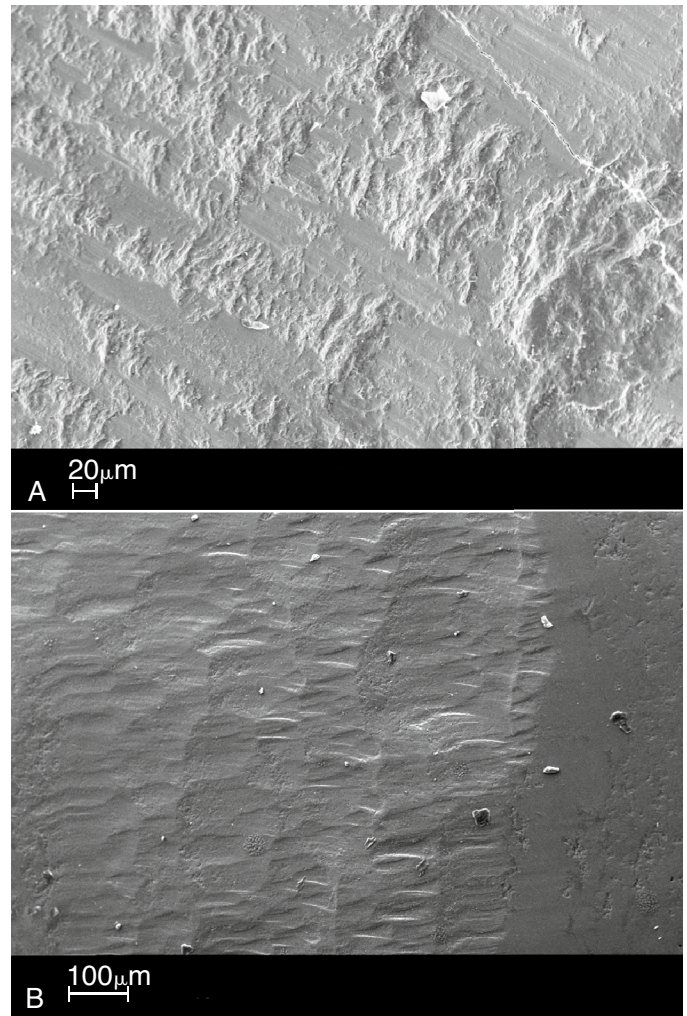


• **Figure 16-20** Wear facet of a milled and glazed ceramic after wear simulation. **A**, Three-dimensional image generated with FRT MicroProf sensor. **B**, A scanning electron micrograph ($\times 100$). (Courtesy Dr. Siegwad Heintze.)

heat and vibration, there is relatively little potential for tooth chipping or microfracturing. These systems have been extended to the following applications: endodontic access through porcelain crowns, minimal preparation for crown margin repair, tunnel preparations, superficial removal of stains, cleaning of tooth surfaces before adhesive bonding, and roughening of internal surfaces of indirect porcelain or composite restorations before adhesive bonding.

Prophylaxis Paste Selection for Dental Hygiene Procedures

The composition and particle size of abrasives contained in various prophylaxis pastes can have adverse effects on exposed cementum and dentin surfaces and esthetic restorative materials. Table 16-3 shows the mean roughness values obtained



• **Figure 16-21** Scanning electron micrograph images of enamel stylus. **A**, Abraded by glazed crowns. **B**, Abraded by optimally polished crowns. (Courtesy Dr. Siegwad Heintze.)

TABLE 16-3 Effect of Prophylaxis Pastes on Glazed Ceramic Surface Roughness

Product	Surface Roughness
Proxylt coarse (Ivoclar Vivadent, Amherst, NY)	0.183 ± 0.08
Proxylt fine (Ivoclar Vivadent, Amherst, NY)	0.066 ± 0.03
Nupro coarse (Dentsply International, York, PA)	0.209 ± 0.11
Nupro fine (Dentsply International, York, PA)	0.188 ± 0.07
Control (glazed surface)	0.061 ± 0.03

on glazed ceramic surfaces after three rounds of 10-second application of various prophylaxis pastes by the same operator. Only one of the pastes (Proxylt Fine, Ivoclar Vivadent, Amherst, NY) did not alter the surface smoothness significantly. Similarly, another study revealed the effect of the same prophylaxis pastes on the gloss reduction of a polished resin composite (Table 16-4).

Air-particle abrasion has been adapted for removing plaque and stains from tooth surfaces using a sodium bicarbonate

slurry; the process is called *air polishing*. Air-particle abrasion is more efficient and effective compared with the technique using a rubber cup and prophylaxis paste because air polishing can access more tooth surfaces. However, softer restoration surfaces, such as glass ionomer, can be damaged. Therefore air polishing should be used with caution around cosmetic restorations.

TABLE 16-4 Effect of Prophy Pastes on Polished Composite Surface Gloss Reduction, Measured by Gloss Units, After a 60-Second Application

Product	Mean GU \pm SD
Nupro coarse	-40.86 ± 4.22^a
Nupro fine	-40.57 ± 5.64^a
Proxyl coarse	-41.61 ± 3.32^a
Proxyl fine	-16.24 ± 3.34^b

GU, gloss unit; SD, standard deviation.
The difference between mean values of groups represented by the same superscripts is not statistically significant.

Dentifrices

Tooth-cleaning substances, such as dentifrices, are available as toothpastes, gels, and powders. Dentifrices have three important functions: (1) Their abrasive and detergent actions provide more efficient removal of debris, plaque, and stained pellicle compared with the use of a toothbrush alone; (2) they polish teeth to provide increased light reflectance and superior esthetic appearance, and the high polish, as an added benefit, enables teeth to resist the accumulation of microorganisms and stains better than rougher surfaces; and (3) they act as vehicles for the delivery of therapeutic agents with known benefits—for example, anticaries agents, desensitizing agents, antimicrobial agents, and antitartar agents.

Dentifrice Composition

Typical components of dentifrices, along with specific materials used and purpose, are listed in Table 16-5. The abrasive concentrations in paste and gel dentifrices are lower than those of powder dentifrices. Therefore powder dentifrices should be used more sparingly and with greater caution by patients, especially where cementum and dentin are exposed, to avoid excessive dentinal abrasion and pulpal sensitivity.

Desensitizing agents in toothpastes work by either depolarizing nerve endings to reduce the transmission of pain, such as with potassium nitrate, or by blocking dentinal tubules, such as with stannous fluoride, sodium fluoride, and strontium chloride.

TABLE 16-5 Typical Dentifrice Components*

Component	COMPOSITION (wt%)		Materials	Purpose
	Pastes and Gels	Powders		
Abrasive	20–55	90–98	Calcium carbonate Dibasic calcium phosphate dihydrate Hydrated alumina Hydrated silica Sodium bicarbonate Mixtures of listed abrasives	Removes plaque or stain Polishes tooth surface
Detergent	1–2	1–6	Sodium lauryl sulfate	Aids in debris removal
Colorants	1–2	1–2	Food colorants	Are used for appearance
Flavoring	1–2	1–2	Oils of spearmint, peppermint, wintergreen, or cinnamon	Provides flavor
Humectant	20–35	0	Sorbitol, glycerine	Maintains moisture content
Water	15–25	0	Deionized water	Acts as suspension agent
Binder	3	0	Carrageenan	As thickener, prevents liquid–solid separation
Fluoride	0–1	0	Sodium monofluorophosphate Sodium fluoride Stannous fluoride	Prevents dental caries
Tartar control agents	0–1	0	Disodium pyrophosphate Tetrasodium pyrophosphate Tetrapotassium pyrophosphate	Inhibits formation of calculus above the gingival margin
Desensitization agents	0–5	0	Potassium nitrate Strontium chloride, stannous fluoride	Nerve desensitizing agent Promotes occlusion of dentinal tubules

*Some compositional information provided by Dr. George Stookey.

Antimicrobial agents such as stannous fluoride and triclosan reduce gingivitis. Products advertised as “whitening toothpastes” typically contain hydrogen peroxide or carbamide peroxide to bleach intrinsic stains as an added benefit to the surface-stain-removal mechanism of any abrasive present.

Dentifrice Abrasiveness

Dentifrices do not have to be highly abrasive to clean teeth effectively. This is important because exposed root-surface cementum is abraded at a rate of 35 times and dentin at 25 times the rate of enamel. The preferred means of evaluating dentifrice abrasiveness is to employ irradiated dentin specimens and brush them for several minutes with test and reference dentifrices. An abrasiveness ratio is calculated by dividing the amounts of radioactive phosphorus (P^{32}) released from the test dentifrice with that from the reference dentifrice, and this value is multiplied by 1000. A test dentifrice must obtain an abrasiveness score of 200 to 250 or less to satisfy the abrasiveness test requirements proposed by the American Dental Association (ADA) and the International Organization for Standardization (ISO). This means that a test dentifrice must abrade dentin at 20% to 25% of the rate of the reference standard to be considered safe for normal usage. A problem with this laboratory test is that the test does not account for all variables that would affect abrasiveness under in vivo conditions. Some of the factors affecting dentifrice abrasiveness are listed in Box 16-1.

Another problem is that not all dentifrices respond in a similar manner under this test. Therefore, using this laboratory test

Box 16-1 Factors Affecting Dentifrice Abrasiveness

Extraoral Factors

Abrasive particle type, size, and quantity in dentifrice
Amount of dentifrice used
Toothbrush type
Toothbrushing method and force applied during brushing
Toothbrushing frequency and duration
Patient's coordination and mental status

Intraoral Factors

Saliva consistency and quantity (normal variations)
Xerostomia induced by drugs, salivary gland pathology, and radiation therapy
Presence, quantity, and quality of existing dental deposits (pellicle, plaque, calculus)
Exposure of dental root surfaces
Presence of restorative materials, dental prostheses, and orthodontic appliances

to predict the in vivo abrasiveness of various dentifrices is very difficult or impossible. However, the majority of modern dentifrices are not exceedingly abrasive. Patients should experience similar amounts of relative wear from the various dentifrices as those found in laboratory tests. In fact, one published document

Selected Readings

- Fruits TJ, Miranda FJ, Coury TL: Effects of equivalent grit sizes utilizing different polishing motions on selected restorative materials, *Quintessence Int* 27:279–285, 1996.
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- This publication thoroughly describes the scientific basis of friction, wear, and lubrication.

rated four dozen dentifrices with regard to cleaning ability and abrasiveness. The products are ranked as high, moderate, or low in abrasiveness. That most of the evaluated products meet the American National Standards Institute (ANSI)/ADA and ISO test requirements is highly probable. Thus these rankings should be considered a guide to products that do not exceed a maximum acceptable (safe) abrasiveness value.

Toothbrushes

The bristle stiffness of toothbrushes alone has been shown to have no effect on the abrasion of hard dental tissues. However, when a dentifrice is used, there is evidence that more flexible toothbrush bristles bend more readily and bring more abrasive particles into contact with tooth structure, albeit with relatively light forces. This interaction should produce more effective abrasion and cleaning action on the areas that the bristles can reach. Battery-powered toothbrushing devices provide a variety of cleansing actions that are claimed to improve tooth-cleaning actions over those achieved by manual toothbrushes.

Summary and Recommendations

Lab technicians, dentists, and dental hygienists should carefully select the appropriate abrasive system for each restoration. Although using the same instruments for grinding and finishing different materials is convenient, the quality of the finished tooth or material surfaces may be far less than ideal if the optimal processes and abrasives recommended for specific materials are not followed. For in vivo processes, use liquid coolant, whenever possible. In situations where a copious supply of liquid coolant is not possible, intermittent application of polishing pressure should be performed.

Change the orientation of the polishing path from one abrasive step to the next as successively finer and finer abrasives are used. Use lighter pressure as the final stages of each abrasive step are reached. The same grit, applied with lighter pressure, can produce a slightly finer surface. Ideally, use separate polishing instruments or carriers (e.g., brushes or rag wheels) for each abrasive grit. Completely removing all coarse abrasive particles from an instrument then reliably using the same instrument for a finer abrasive is difficult, if not impossible. Inevitably, scratches from stray coarse abrasive particles can occur. Similarly, thoroughly clean coarser abrasives from restorations before moving to finer abrasives. Rinse treated surfaces periodically to remove wear debris that may interfere with the ability to produce the finest possible surface finish.

Acknowledgment

The contributions of Dr. Kenneth Anusavice and Dr. Sibel Antonson to the development of this chapter in the 11th and 12th editions are appreciated.

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- The tactile ability of the tongue to discern very small changes in surface roughness intraorally are suggested in this study.
- Kroschwitz JI, Howe-Grant M, editors: *Kirk-Othmer Encyclopedia of Chemical Technology*, ed 4, vol 1, New York, 1991, Wiley, pp 17–37.
- This encyclopedia presents a thorough review of specific abrasives, their physical properties, and their methods of manufacture.

Lawson NC, Janyavula S, Syklawer S, et al: Wear of enamel opposing zirconia and lithium disilicate after adjustment, polishing and glazing, *J Dent* 42:1586–1591, 2014.

This article shows that polished zirconia wears less and polished lithium disilicate wears equivalent to natural enamel. Glazes should not be applied to contacting surfaces.

Mackert JR: Side effects of dental ceramics, *Adv Dent Res* 6:90–93, 1992.

This article presents information on silicosis and the potential hazards of porcelain dust generation during grinding procedures.

Nakazato T, Takahashi H, Yamamoto M, et al: Effects of polishing on cyclic fatigue strength of CAD/CAM ceramics, *Dent Mater J* 18:395–402, 1999.

Powers JM, Bayne SC: Friction and wear of dental materials. In Henry SD, editor: *Friction Lubrication and Wear Technology, ASM Handbook*, vol 18, Materials Park, OH, 1992, American Society of Metals International, 1992, pp 665–681.

This article, a compilation of information from more than 200 sources, presents a review of friction and wear as they relate to human dental tissues and restorative materials.

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This abstract outlines the study showing the effect of different prophylactic pastes on the gloss of resin composite.

17

Biocompatibility

OUTLINE

Basic Concept of Biocompatibility

Biological Effects From Exposure to Dental Materials

Occupational Hazards for Dental Personnel

Biocompatibility Testing

Legal Regulations and Risk Classes

Side Effect of Various Material Groups

Patient Reports and Complaints of Adverse Effects

Clinical Guidelines for Selecting Biocompatible Materials

Acknowledgments

KEY TERMS

GENERAL

Adverse reaction Any unintended, unexpected, and harmful response of an individual to a (dental) treatment or biomaterial.

Bioactive materials Biomaterials that, in addition to their primary function (e.g., to restore dental hard tissues), actively stimulate a specific positive tissue response or control their microbiologic environment.

Biocompatibility The ability of a biomaterial to perform its desired function with respect to a medical (or dental) therapy, without eliciting any undesirable local, allergic, or systemic effects in the recipient or beneficiary of that therapy but generating the most appropriate beneficial cellular or tissue response in that specific situation and optimizing the clinically relevant performance of that therapy.

Biointegration The process of forming an interface between bone or other living tissue and an implanted material with no intervening space. Biocompatibility is a prerequisite for biointegration.

Osseointegration The process of forming a direct structural and functional interface between live bone and an artificial implant surface without any intervening fibrous connective tissue. Biocompatibility is a prerequisite for osseointegration.

Risk Combination of the probability of harm to health occurring as a result of adverse reactions associated with a biomaterial interaction and the severity of that harm.

Safety The absence (freedom) from unacceptable risks in the context of the intended use.

Xenoestrogen A chemical that is not indigenous to the body but acts in a manner similar to that of estrogen.

BIOLOGICAL OR CLINICAL EFFECTS

Allergy A clinical hypersensitivity reaction initiated by specific immunological mechanisms.

Carcinogenicity Malignant tumor formation caused, for example, by an exposure to a chemical or biomaterial.

Cytotoxicity Cell death or impairment of cell metabolism caused by an exposure to a chemical or biomaterial.

Estrogenicity Body reaction in a manner similar to that of estrogen, the female sex hormone, from exposure to a chemical or biomaterial.

Genotoxicity A change of the DNA or of chromosomes caused, for example, by an exposure to a chemical or biomaterial.

Hypersensitivity The objectively reproducible symptoms or signs initiated by an exposure to a defined stimulus at a dose tolerated by normal persons.

Mutagenicity A change of the DNA or of chromosomes, which is transferred to the next cell generation, caused, for example, by an exposure to a chemical or biomaterial.

Sensitization The process by which antibodies or specific immune cells are produced, which react specifically to the causative foreign substance.

Toxicity The relative ability (dose-related effect) of a substance or a material to cause injury to biological tissues, ranging from improper biochemical function, organ damage, and cell destruction to death. Depending on the duration of exposure period, the terms *acute toxicity* (≤ 24 hours), *subacute toxicity* (> 24 hours but ≤ 30 days), and *chronic toxicity* (> 30 days) are used.

LIMIT VALUES

Lethal dose fifty (LD₅₀) The calculated dose of a substance that is expected to cause the death of 50% of the entire population of a biological collective, such as specific experimental animals or cells.

No-observed-adverse-effect level (NOAEL) The highest tested dose of a substance that has been reported to have no harmful (adverse) health effects on people, animals, or cells.

Since ancient times, a wide variety of materials have been placed or implanted in humans to replace or repair missing, damaged, or defective body tissues. Animal bones, seashells, animal teeth, human teeth, metals, resin materials, and inorganic compounds are materials that have been used for restoration of damaged or decayed teeth or replacement of missing teeth. The outcomes of these interventions have varied from short-term failure to limited success in certain individuals. Many of these treatments reflected situations in which the risks were far greater than the anticipated benefits. Some of these materials have caused immediate or delayed **adverse reactions** because of their allergenic or toxic potentials. On the other hand, some materials appear to evoke a minimal biological response but seem to interact with the host tissue harmoniously. Thus the term *biocompatible* evolves.

Basic Concept of Biocompatibility

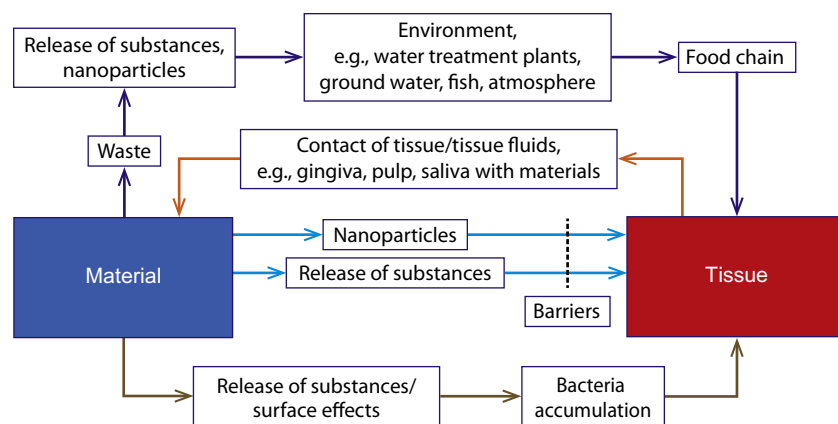
Biocompatibility is related to the fact that a (dental) material that is placed on or in parts of the human body comes into close contact with living tissue, with the consequence of an interaction between the material and the tissue. This interaction is primarily based on the substances that are eluted (i.e., released) from the material when in contact with various tissues; released substances then in turn influence the living tissues (Figure 17-1). Furthermore, such released substances can influence the surrounding microbiota (e.g., biofilms), which then indirectly affects the tissue, such as inducing a bacterial inflammation. Nanoparticles originating from dental materials during processing (grinding or polishing) or during restoration removal can also interact with cells. Finally, the influence of disposing dental material wastes to the environment has gained increased concern. For example, amalgam debris discharged from dental offices enters water treatment plants and then landfills as sewage waste. The mercury in amalgam is released to ground water or air and eventually enters the food chain, which may influence human health. Thus the primary purpose of characterizing the biocompatibility of dental materials is the protection of the patient, the dental personnel, and the environment.

The adverse effects of a material lead to the awareness of biocompatibility. Adverse reactions caused by dental restorative materials can be classified into three groups: systemic effects, local effects, and allergies. *Systemic effects* are those where the site of application

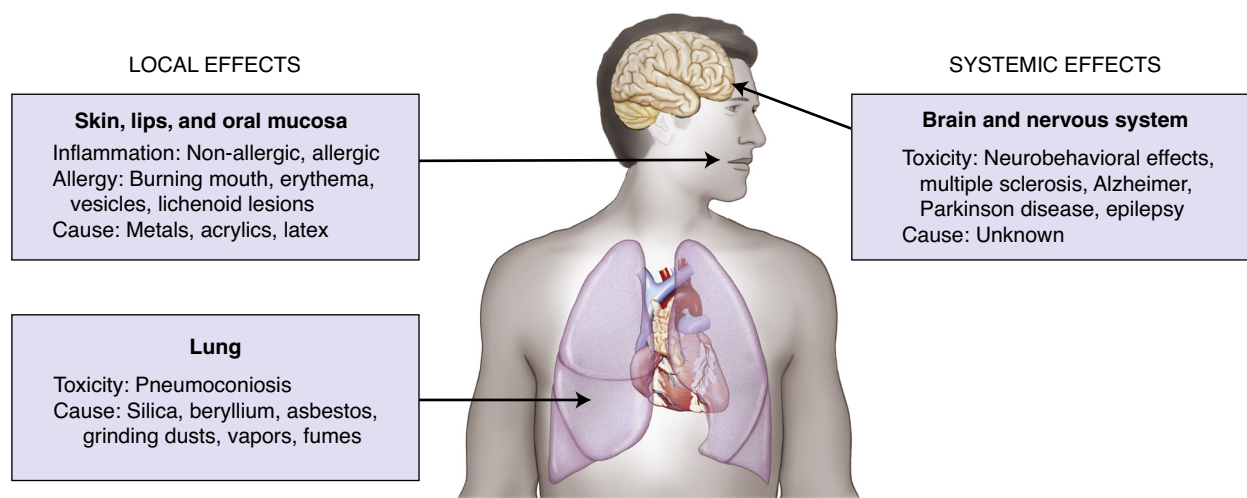
is distant from the site of action. For example, mercury vapor from amalgam fillings reaches different organs through inhalation and then the bloodstream, with (claimed) adverse effects at these organs (Figure 17-2). *Local effects* occur in the direct vicinity of the material applied. This can be an inflammation of the dental pulp after placement of a resin-based composite restoration in a deep cavity or inflammation of the gingiva next to a resin-based restoration (Figure 17-3) or a metal prosthesis (Figure 17-4). **Allergies** are based on an immunological antibody–antigen reaction leading to a number of clinical symptoms that occur more frequently than systemic effects. The adverse effects are discussed in detail in the next section.

Bioactivity can be regarded as an intended positive local effect of dental materials in addition to their primary function (e.g., to restore dental hard tissues). The term *bio* means “life/living.” Therefore bioactive effects are primarily related to material-induced and cell-mediated effects on living tissues like the dental pulp. Examples are the induction of new dentin formation by calcium hydroxide products. Also, antimicrobial activity may be regarded as a bioactive effect. Some manufacturers and authors broaden the term bioactivity to include a mainly inorganic chemically induced remineralization of dental hard tissues or the formation of an apatite-like substance on the surface. Therefore materials that release Ca^{2+} , $(\text{PO}_4)^{3-}$, or F^- , which are necessary components for forming apatite, are termed **bioactive materials** or *smart materials* by manufacturers. The clinician should be critical and ask for actual clinical evidence of such claims based on clinical studies and ensure that the necessary properties of the restorative materials for fulfilling their primary use are not impaired as a result of the release of molecules.

In daily life, the assessment of the biocompatibility of dental materials is often expressed in terms of **risk** and **safety**. “Safety” in layperson terms is often meant to describe a situation where harm will *never* happen. But such an “absolute safety” is not possible. There is always a chance, however small it may be, that an adverse event may happen. Interestingly, high-risk activities, such as mountain climbing, are engaged in by patients without any major concern, but the same patients are afraid of certain dental materials (e.g., amalgam) or of certain procedures (e.g., dental x-rays). This indicates that the risk perception of the patient is purely intuitive, and it is not related to the actual risk. The



• **Figure 17-1** Basic concept of the interaction of dental materials with tissues. Orange arrows indicate the action of the tissues on the material. Cyan arrows show the action of the materials/their eluates on the tissues, and brown arrows show the bacteria-mediated interaction. Blue arrows indicate the effect of materials on the environment, which then also may influence human health. (Adapted from Schmalz G, Galler KM: Biocompatibility of biomaterials, *Dent Mater* 33:382–393, 2017.)



• **Figure 17-2** Schematic illustration of critical tissues and organs that may be susceptible to the adverse effects of dental materials.



• **Figure 17-3** Inflammatory response or possible allergic reaction adjacent to a Class V resin-based composite. However, no patch test was performed to confirm an allergy as the cause of this inflammation. (Courtesy Dr. Hyun-Ju Chung.)



• **Figure 17-4** Inflammatory response adjacent to a crown (lower right) made from a metal coping. No definitive diagnosis can be made of potential allergens. Thorough dental and medical histories and patch testing are required for the evaluation of this condition. (Courtesy Dr. Hyun-Ju Chung.)

actual risk is the combination of the probability and the severity of harm that can be evaluated according to ISO 14971:2019, Medical Devices—Application of Risk Management to Medical Devices. Therefore, when informing the patients about possible adverse effects from dental materials, the clinician must consider the difference between the public's perception and the measurable estimation in terms of risk and safety by ISO 14971:2019.

Finally, risk versus benefit has to be assessed before a material is allowed to be sold on the market. Dental (and medical) materials are used to diagnose, prevent, and alleviate disease (e.g., caries) or restore lost teeth structure. An example is mercury, which is an element that is poisonous to human health and has been used to form amalgam as a dental restoration for restoring function of teeth damaged by caries. However, mercury should not be used in shoes to switch on lights for fun.

CRITICAL QUESTIONS

Why might the local response and the systemic response to a dental material differ? Which factors come into play to explain these differences?

Biological Effects From Exposure to Dental Materials

There are five main pathways through which harmful substances can enter the body: (1) absorption through skin/mucosa/dentin and eye contact, (2) leakage through the tooth apex, (3) direct contact with bone (implants), (4) inhalation, and (5) ingestion. Keep in mind that skin, mucosa, and dentin act as a (partial) barrier against the entry of foreign substances into the body. If this protective barrier is broken by abrasions or lacerations, toxic substances can penetrate the barrier and migrate into the body. In addition, exposure to some organic solvents or inorganic acids can increase the permeability of the skin, mucosa, and dentin. The fastest way for toxic substances to enter the body is through inhalation (Figure 17-2) or in direct contact with bone. Inhaled vapors or particulate matter can make immediate contact with respiratory tissues and soon thereafter make contact with the bloodstream. Once a substance has entered the bloodstream, this substance is transported rapidly throughout the body.

Systemic Effects of Materials

Systemic effects from dental materials are a function of the distribution of substances released from dental materials in the body. Their migration to other sites of the body can occur by diffusion through tissues or by flow through lymphatic channels or blood vessels. The ultimate systemic response depends on six key variables: (1) site of exposure, (2) the intrinsic (i.e., molecular) **toxicity**, (3) the effective concentration of the substance at the site of action, (4) the time of exposure, (5) the excretion rate of the substance, and (6) the target organ (site of action). When substances are excreted slowly, their critical concentrations are reached more rapidly than are those concentrations of substances that are excreted quickly.

CMR Effects

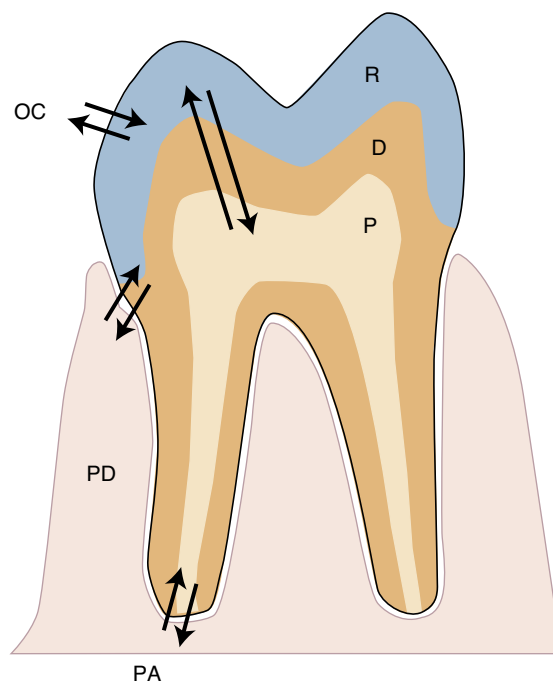
The term *CMR effects* refers to carcinogenicity, mutagenicity, and reproductive toxicity. Any adverse effect on the DNA of an organism caused by a chemical or a material is termed **genotoxicity**. If the adverse effect is transferred to the next (heritable) generation of cells, the effect is called **mutagenicity**. Thus genotoxicity can be regarded as the first and necessary step for mutagenicity. Genotoxic reactions occur when a physical or chemical agent changes the genetic material of an organism. Mutations are common occurrences in the DNA of all humans, and they may result from many factors, such as radiation, genotoxic chemicals, and genetic errors in the DNA replication process. Several metal ions, such as beryllium, cobalt, and nickel, are known mutagens. Some components in root canal sealers and resin-based materials have exhibited mutagenic potential in vitro. Mutagenicity does not have the same consequences as carcinogenicity, and many mutations are repaired. Others are irrelevant or insignificant, or the affected cell undergoes apoptosis, preventing the transfer of the DNA damage to the next cell generation. No dental material has ever been shown to be carcinogenic in dental patients. Reproductive toxicity plays virtually no role in dental materials but has to be considered during preclinical risk assessments performed by the manufacturer.

Estrogenicity

Estrogenicity is the ability of a chemical to act as the hormone estrogen does in the body. If these chemicals are not indigenous to the body, the substances are called **xenoestrogens**. In 1996 Olea et al. claimed that dental sealants released estrogenic substances in sufficient quantities to warrant concern. The compound of concern is called *bisphenol-A (BPA)*, which is a precursor of the bisphenol-A glycidyl dimethacrylate (*bis-GMA*) monomer widely used in the formulation of dental composites and sealants and a building block of plastics like the polycarbonates used in some orthodontic brackets. BPA is a known xenoestrogen. The fear is that the release of these substances from dental materials will compound exposure to other (nondental) sources of endocrine disruptors, which in turn may lead to (claimed!) diseases such as type 2 diabetes, obesity, premature puberty, and even (breast) cancer, albeit such claims are highly controversial. The amounts of BPA released from dental resin composites are very low. Therefore the estrogenicity of dental composites has also been questioned, particularly for use in children. For more details, see the discussion on resin-based composites.

Local Effects of Materials

The arrows in **Figure 17-5** indicate the pathways that foreign substances from a restorative material can take leading into the oral cavity (OC), the tissue space next to the periodontium (PD), the



• **Figure 17-5** Schematic illustration of pathways that leached ions or substances may follow during in vivo degradation of a dental restoration (R) into the oral cavity (OC), dentin (D), the pulp chamber and the pulp tissue (P), the periodontium (PD), and periapical tissue and bone (PA).

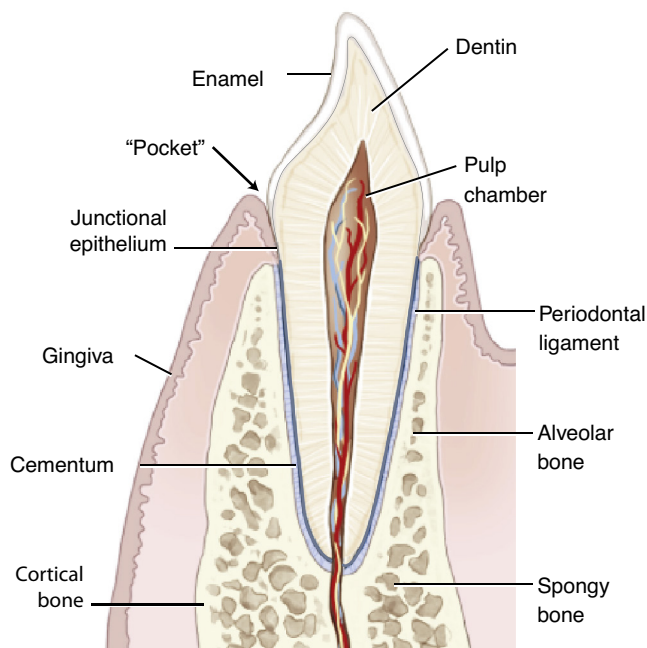
pulp chamber (P), or the periapical region (PA). Local effects that occur on nearby oral tissues such as the buccal mucosa, the periodontium, or tongue are generally apparent to visual inspection. Local effects also occur, often hidden from our eyesight, including in the pulp tissue, tooth–restoration interfaces, and bone–implant interfaces.

Pulp Tissue

Postoperative discomfort/sensitivity or pain, which may occur shortly after the treatment with dental restorative materials, may result from several factors, including thermal trauma, chemical injury, microleakage, and allergy. The perception of this postoperative sensitivity is generally believed to be related to the movement of extracellular fluid in the dentinal tubules and the influence of this fluid movement on the odontoblastic processes, as proposed in the so-called *hydrodynamic theory* of postoperative sensitivity. As a result of this movement, cell receptors on the surface of the odontoblast processes are stimulated, and the odontoblasts transfer this signal to afferent nerves, which are closely associated with the odontoblast layer. Therefore sealing the dentinal tubules during the restorative procedure is clinically important to prevent or reduce intratubular fluid movement and thus postoperative sensitivity.

Pulp damage (inflammation) caused by a restorative material may very often occur without any clinical symptoms at the beginning and is only detected histologically. The intratubular fluid becomes the medium for the diffusion of foreign substances into the pulp chamber. However, the thickness of the remaining dentin between the material and the pulp chamber can slow down the process, and dentinal sclerosis under a carious lesion will further decrease the dentin permeability. Furthermore, dentin may act as a buffer for acidic substances like self-etch adhesives. Therefore dentin can be regarded as a partial barrier. A major problem in the

diagnosis of potential pulp damage caused by a restoration is the fact that there is virtually no correlation between the histologically documented damage to the pulp and clinical symptoms. This is considered a major drawback of clinical studies (without histology) in this area.



• **Figure 17-6** Schematic illustration of the periodontal attachment area. The gingiva is attached to the tooth's cementum surface just below the enamel with a specialized epithelium, which is called the *junctional epithelium*. The periodontal "pocket" is formed from the gingival tissue extension above the junctional epithelium. Cementum covers the dentin, starting at the enamel–dentin junction. Below the gingiva, alveolar bone attaches to cementum through a tissue called the *periodontal ligament*. This ligament is not present when implants are osseointegrated with bone.

Periodontium

The periodontal attachment to the tooth is an important junction between the outside of the body (oral cavity) and the inside of the body (Figure 17-6). The periodontal tissues are targets for possible adverse effects from dental materials because these materials are in close proximity to these tissues. The periodontal pocket, or gingival sulcus, may accumulate biofilms and significant concentrations of ions or molecules of leached substances. Such accumulations can elicit inflammatory reactions such as gingivitis or influence the body's ability to defend against bacteria that cause periodontal disease.

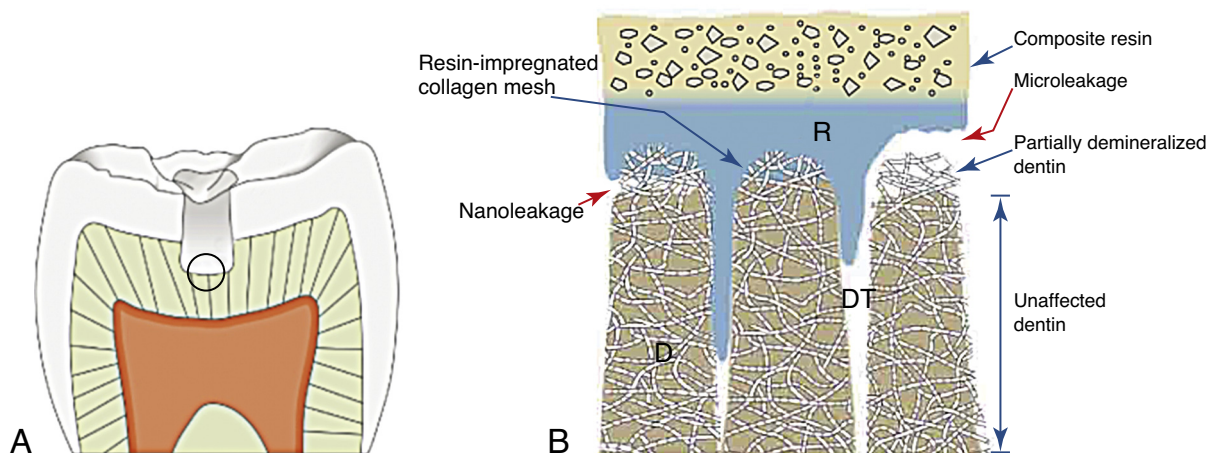
CRITICAL QUESTION

How can microleakage influence the biological response to a material?

Tooth–Restoration Interfaces—Microleakage and Nanoleakage

Dental restorative materials form interfaces with one another (adhesives with resin composites or cements with dental alloys) and with the dental hard tissues. The tooth–restoration interface is critical for the transfer of leached substances into dentinal fluid. As shown in Figure 17-7, debonding of the adhesive layer from the dentin, as a result of, for example, polymerization stress, can lead to fluid ingress along gaps, which leads to so-called microleakage, or the diffusion of bacteria and fluids into this gap. The microscopic gap and the microleakage may lead to several undesirable events. Bacteria may migrate into this gap and may even form a thin biofilm, which then initiates an inflammation of the pulp tissue. The gap also promotes material breakdown and secondary caries along the unsupported margin. This breakdown increases the gap width, which allows larger particles and molecules to progress toward the pulp chamber. The presence of this gap also causes marginal staining and compromised esthetics that may lead to restoration replacement.

If the resin from dental adhesives penetrates the collagen network of the acid-treated dentin but does not penetrate the



• **Figure 17-7** Concepts of microleakage and nanoleakage. **A**, Cross section of Class I composite restoration. **B**, Diagram illustrating the interphase of bonding resins (R) to dentin (D). The dentin has been acid-etched in preparation for the application of the resin adhesive, which leaves the collagenous matrix of the dentin exposed (demineralized dentin). If the resin does not completely penetrate the collagen network (left), then a small space of communication exists between the tubules (DT) and the collagen network (red arrow, left). This situation allows for nanoleakage. On the other hand, if the resin fails to penetrate the collagen network at all, or debonds from it, then the space is much larger (red arrow, right). This situation allows for microleakage. In the ideal situation (center), the resin penetrates the collagen network all the way to the mineralized dentin.

network completely, then a much smaller gap (less than 0.1 μm in most cases) may develop between the mineralized matrix of dentin and the collagen–resin hybrid layer (Figure 17-7). This much smaller gap may lead to nanoleakage, which probably does not permit bacteria penetration but allows fluid exchange that may degrade the resin or the collagen network and subsequently reduce the longevity of the dentin–resin bond.

Micromechanical interlocking occurs between the bonding of resins from dental adhesives to enamel. Enamel does not contain collagens, and the bond to resin is based on the interlocking of the resin with the etched enamel surface and potentially on chemical bonding between the resin and the enamel apatite (for 10-methacryloyloxydecyl dihydrogen phosphate [MDP]-based adhesives). Therefore nanoleakage is not known to occur between restorations and enamel.

Bone–Implant Interface

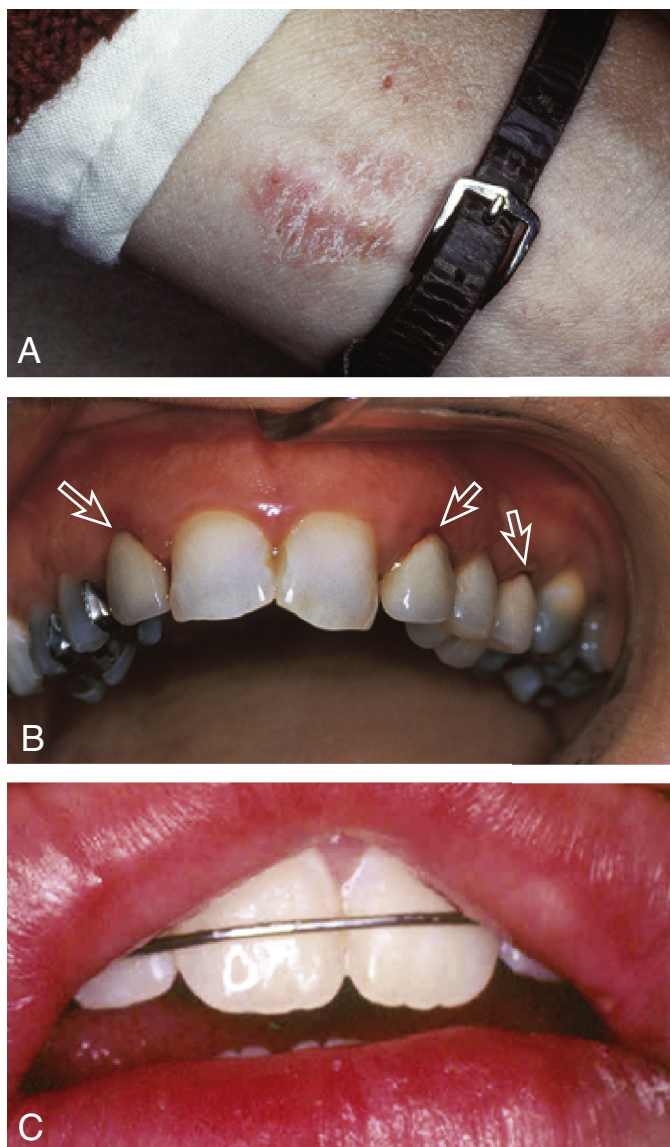
The success of endosseous dental implants depends on the stability of the implant, which is determined by the biomechanical properties of the bone–implant interface. The initial stability is gained from introducing the implant into a prepared cavity slightly smaller than the size of implant, which allows the implants to be threaded into bone. The final stability is achieved by the ingrowth and integration of new bone onto the implant surface through the process of **osseointegration**. Materials that allow osseointegration have very low degradation rates, and they tend to form biocompatible surface oxides that enhance bony approximation. The general process of **biointegration** involves the adaptation of bone or other tissue to the implanted material without any intervening space along the tissue–material interface. The majority of current dental implants are made of commercially pure titanium or titanium alloys (Chapter 12, **Titanium and Titanium Alloys**).

Allergic Reactions

An allergic reaction occurs when the body recognizes a substance, molecule, or ion as foreign, and the human immune system can react specifically even at a very low dose. The reactions are well recognized by the public, but specific allergens are difficult for health care professionals to identify.

There are four types of allergy reactions according to the Gell and Coombs classification of immune responses proposed in 1963. A type I reaction (mediated by immunoglobulin E [IgE] or immunoglobulin G4 [IgG4]) is an immediate hypersensitive reaction or anaphylactic reaction when an antigen interacts with mast cells or basophils. A type II reaction is caused by cytotoxic antibodies, which are primarily immunoglobulin M (IgM) or immunoglobulin G (IgG). A type III reaction involves tissue injury by immune complexes. A type IV reaction is a delayed or cell-mediated **hypersensitivity**, and it is evoked, for example, by metal ions, which, as so-called *haptens*, must first interact with a host molecule (protein) in order to be able to produce a delayed type IV hypersensitivity reaction. This type is often associated with an allergic contact dermatitis. A type V reaction, which is a stimulating antibody reaction, has been suggested but sometimes classified as a subcategory of type II. In dentistry, allergy type IV reactions (delayed type) are generally more frequent than type I reactions (immediate reactions).

Figure 17-8 illustrates three potential sites for allergic reactions to nickel-containing metals: a watchband buckle (Figure 17-8, A); bilateral, fixed metal-ceramic prostheses with copings and



• **Figure 17-8** Various forms of nickel allergy. **A**, Allergic reaction to nickel alloy in watchband buckle. **B**, Bilateral erythema in a female patient that may have been associated with allergic reactions to nickel in a recently cemented metal-ceramic crown (left) and in two metal-ceramic crowns (right) of a three-unit fixed dental prosthesis. **C**, Severe allergic reaction in the lips of a patient who was exposed to a nickel-containing orthodontic wire. (**C**, Courtesy Dr. Donald Cohen.)

framework made from nickel alloy (Figure 17-8, B); and a severe reaction of lips to nickel-containing wire (Figure 17-8, C).

Frequencies

Dental professionals suffer hand dermatitis from frequent hand washing, prolonged glove use, and exposure to skin-irritating and skin-sensitizing chemicals in their working environment, particularly methacrylate-based monomers. In one study, nearly 2% of dental personnel were reported to suffer from methacrylate-caused hand dermatitis. Contact allergy to methacrylate was seen in 22% of the patch-tested persons. Other frequent allergens are nickel, cobalt, palladium, fragrance mix, colophonium, and thiuram mix. Allergy to natural rubber latex was diagnosed in 10% of the dental personnel. In summary, chemical-irritant hand dermatitis was the dominant diagnosis.

Dental patients usually present with different manifestations of the oral mucosa. In a group of more than 4000 people with a clinically suspected allergy against dental materials, the most frequent allergic patch test reactions in the dental screening series were induced by nickel, ammoniated mercury, metallic mercury, gold, benzoic acid, palladium, cobalt, and 2-hydroxyethyl methacrylate (HEMA). Moreover, triethylene glycol dimethacrylate (TEGDMA) was found to be a frequent sensitizer. Other studies have reported chromium and indium as allergens. Positive reactions to metals were frequent in patients with different symptoms, and no specific association between a specific clinical presentation and a particular allergen was found.

A maximal frequency of 0.3% for any adverse effect and for all dental materials has been reported, meaning the frequency of just allergic reactions of patients may be even lower. Within the group of patients claiming that their subjective complaints or objective symptoms are the result of applied dental materials, the rate of allergic reactions was found to range between 10% and 14%. Within another group of patients who also exhibit clinical symptoms of an allergy (see following discussion), the rate of positive patch tests (i.e., verification of an allergy) was between 40% and 60%.

Symptoms

For dental personnel with a verified allergy to dental materials, the symptoms found among 174 cases were hand eczema (63%), irritant contact dermatitis (67%), and allergy-induced contact dermatitis (33%). Further diagnoses included other eczemas, urticaria, rosacea, psoriasis, tinea pedis, and bullous pemphigoid.

Exposure of patients to dental materials and other products can elicit symptoms such as burning, tingling, cheilitis, and oral lichenoid contact lesions, as well as swelling of the face, lips, tongue, palate, and buccal mucosa. Between 2000 and 2004, patch tests of 121 patients aged 20 to 80 years revealed that the most frequent oral manifestations were cheilitis and perioral dermatitis (25.6%), burning mouth (15.7%), lichenoid contact reaction (14.0%), and orofacial granulomatosis (10.7%). Dental personnel, representing 18 (14.9%) of the 121 patients, all suffered from hand dermatitis.

Intraorally, so-called *lichenoid contact lesions* (Figure 17-9) have been associated with an allergic reaction to amalgam and dental alloys. Also, other causes, such as mechanical irritation, have, however, been considered as a cause for such contact lesions. The generalized oral lichen planus is not associated with an allergy.

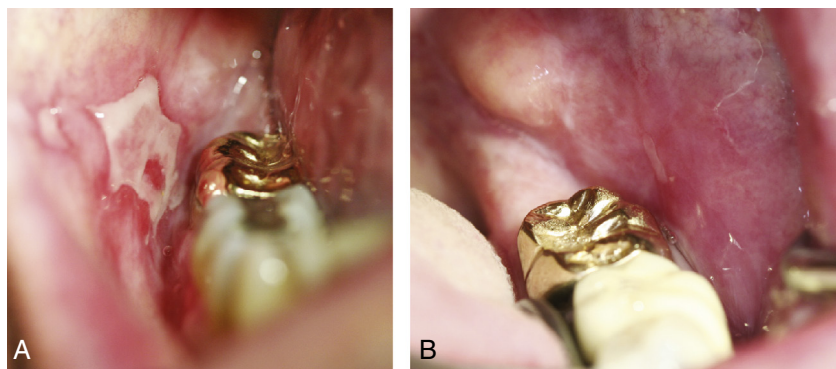
An allergic reaction only occurs after the patient has been sensitized during a first contact by developing antibodies or immune

cells specifically directed to this substance. After **sensitization** to the particular substance, even a brief contact with that allergen may cause the allergic reaction to appear. Dental materials mainly elicit delayed-type reactions (type IV), occurring within 24 to 48 hours or even later. A typical type IV reaction to dental materials is contact dermatitis. One of the most common signs is a change in the color of the skin/mucosa, which usually appears on the spot that was in contact with the material. Other areas of the body can exhibit signs after the initial reaction has occurred. The general signs of contact allergies include (1) reddish, itchy, swollen skin; (2) vesicles; (3) scaly areas; (4) darkening of affected tissue; (5) leathery skin; and (6) cracked skin. The best “cures” for these reactions are avoidance of the suspected materials.

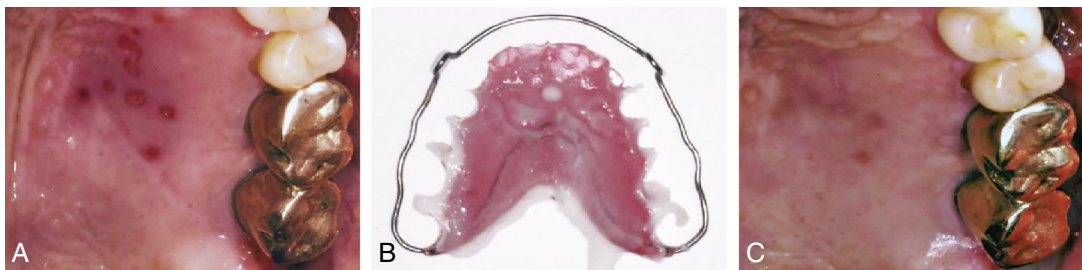
Inflammation

Inflammation may result from microbes/biofilms, trauma (i.e., excessive force, laceration, and abrasion), allergy, or toxicity. Histologically, the inflammatory response is initially characterized by edema of the tissue and by an infiltration of inflammatory cells such as neutrophils and, later in the chronic stage, by the action of monocytes/macrophages and lymphocytic cells. For the clinician, it is important to identify the reason for an apparent inflammation in order to be able to correctly treat the patient.

A rather frequent reason for an inflammation of the oral soft tissues/oral mucosa is bacterial biofilms on or under a dental material. Antibacterial treatment comprises mechanical cleaning of teeth and possibly removable prostheses, improving the patient's own oral hygiene measures, and the use of antiseptic mouth rinses. If the inflammation subsides, bacterial biofilm can be regarded as the reason for the inflammation. If the inflammation persists, and the suspected material is part of a removable prosthesis, this prosthesis should be removed from the mouth for 1 or 2 weeks (elimination test). If the inflammation subsides and reappears after insertion, an allergy can be suspected, and a patch test should be initiated. Figure 17-10 shows an erythematous reaction caused by an acrylic appliance that subsided 2 to 3 days after removal of the appliance. The same is true if inflammation persists after antimicrobial treatment and the material cannot be removed from the mouth. Other material-associated soft tissue inflammations are caused by marginal discrepancies of metallic fixed prostheses (Chapter 9, *Manipulation of Base-Metal Alloys*) and ill-fitting removable prostheses (Chapter 11, *Allergic Reactions*). Gingivitis adjacent to metal-ceramic crowns may also be caused by insufficient removal of metal oxides after the firing



• **Figure 17-9** Bilateral localized lichenoid lesions that are associated with gold alloy crowns. **A**, Lichenoid mucositis lesion (white area) in tissue adjacent to a gold alloy crown. **B**, Lichenoid mucositis lesion in vestibular tissue next to gold alloy crown on opposite side of the arch. Patch testing of the patient was not performed. (Courtesy Dr. Donald Cohen.)



• **Figure 17-10** Erythematous reaction sites. Patch testing was not performed to confirm a suspected allergic response. **A**, Palatal area that was exposed to an acrylic palatal appliance. **B**, Acrylic appliance with embedded wire. **C**, Initial healing of palatal tissue shown in **(A)** within 2 to 3 days after removal of the palatal appliance. (Courtesy Dr. Byung-Gook Kim.)



• **Figure 17-11** Inflammation adjacent to the metal margin of a metal-ceramic crown. A potential allergy to one of the metal components should be explored by a patch test. Furthermore, gingival reactions to metal oxides that were produced during the firing process for metal-ceramic crowns have also been proposed. (Courtesy Dr. Hyun-Ju Chung.)

process (Figure 17-11). In those cases, the prostheses are adjusted or remade to eliminate the inflammation.

CRITICAL QUESTION

What is the task of the clinician when an allergy is suspected?

Patch Test

A patch test is only indicated for patients who exhibit clinical symptoms suspected to be a type IV allergy. Because this type of allergy is most prominent for dental materials, the patch test is mainly performed to verify the allergenic nature of the clinical symptoms. A series of substances, which are suspected to cause the allergy, is placed on the back of the patient in tiny reservoirs and covered by a patch. Figure 17-12 illustrates positive responses of dental alloys on a patient's back. Patch testing in general has been validated for epidermal exposure, which may also induce sensitization of naive T lymphocytes and is relevant primarily for detecting dermal effects of hypersensitivity (contact dermatitis). In vitro testing, for example, with the lymphocyte transformation test (LTT), has been proposed but so far has not found general acceptance by relevant scientific organizations (e.g., American Academy of Allergy, Asthma and Immunology [AAAAI]; see <https://www.aaaai.org/ask-the-expert/lymphocyte>).



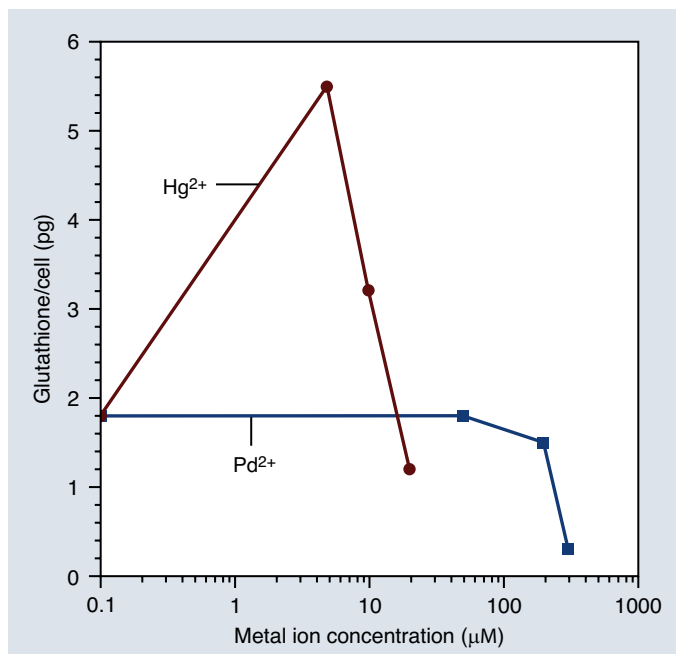
• **Figure 17-12** Positive responses to patch tests on a patient's back. (Courtesy Dr. Young Ho Won.)

All testing for verifying allergies has to be performed by an allergologist, and the referring dentist must provide a list of suspected substances. Tests may be performed with samples of the suspected material (e.g., the alloy) or with the components, such as the cations from metals that are components of the alloy. The use of metal cations and monomers is generally more sensitive than using material samples and is the standard procedure. Therefore information on the composition of the used materials is essential (see the Safety Data Sheets section later in the chapter).

Immunotoxicity

The principal concept of immunotoxicity is that substances can alter the immune system. These cellular alterations can occur because of the direct toxic effect of a leached substance. Monocytes/macrophages control chronic inflammatory and immune responses, and they also secrete many substances, such as signaling molecules, that alter the actions of other cells. Thus, if substances leached from a biomaterial reduce the monocyte's ability to secrete these substances, this may impair the immune system.

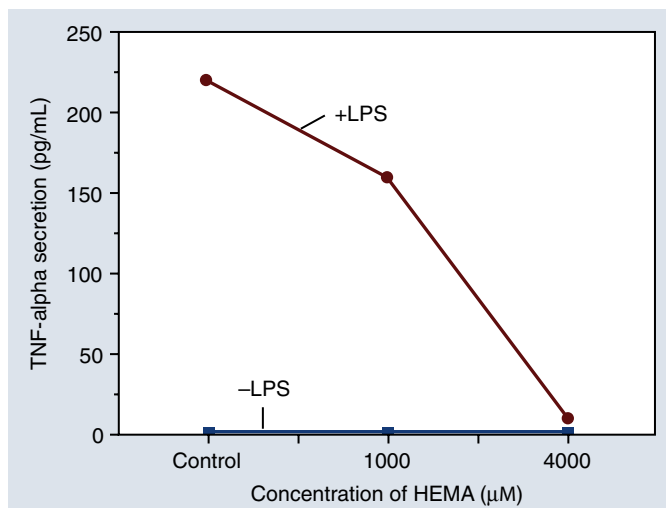
Released substances from dental materials, such as metal ions or monomers, can also alter the immune system at subtoxic concentrations. As shown in Figure 17-13, mercury ions increase the glutathione (GSH) content of human monocytes in cell culture, whereas palladium ions decrease the cells' GSH content. GSH



• **Figure 17-13** Response of monocytes in a cell culture after a 24-hour exposure to mercury ions (Hg^{2+}) or palladium ions (Pd^{2+}). Mercury ions produced a spike in glutathione at an ion concentration of about $8 \mu\text{mol/L}$ and a subsequent decrease as mercury became toxic to the cells. In contrast, during exposure to palladium ions, the glutathione content did not decrease significantly until the palladium ion concentration increased to between 200 and $300 \mu\text{mol/L}$, which is far below the ion concentrations required to induce toxicity in these cells. Because both types of metal ions alter the chemical defense (glutathione production) against oxidative stress at subtoxic ion levels, these metals are believed to affect the immune system. (Courtesy Dr. John Wataha.)

is a tripeptide and is necessary for maintaining the redox balance in cells because GSH compensates for the constantly and physiologically generated reactive oxygen species (ROS). GSH is also responsible for the detoxification of foreign substances entering the cell. However, if the concentration of the foreign substance is increasing, the cellular GSH is depleted (as a result of the detoxification), and the redox balance is impaired. The consequence is cellular stress as a result of the increased ROS concentration. Thus, necessary cell functions in the immune system are impaired.

A further effect on the immune system is a result of the influence of substances from dental materials on the cellular bacterial defense system. Bacterial surface antigens, such as lipopolysaccharides (LPSs) from gram-negative bacteria or lipoteichoic acid from gram-positive bacteria, are recognized by the immune cell surface receptors of human macrophages, which then, through intracellular signal transduction, results in the release of interleukin-1 (IL-1) or interleukin-6 (IL-6) or tumor necrosis factor alpha (TNF- α). These substances are secreted to induce inflammation, with the aim of eliminating the invading bacteria (bacterial clearance). Figure 17-14 shows a graph of the amount of TNF- α secreted by monocytes after LPS stimulation (control) and after additional exposure to HEMA in different concentrations. Exposure to HEMA clearly reduced the TNF- α secretion and therefore impaired bacterial clearance. The significance of this effect is that the relatively small amounts of HEMA released from, for example, dental adhesives can alter the normal functions of immune cells,



• **Figure 17-14** Reduction in secretion of tumor necrosis factor alpha (TNF- α) by monocytes after exposure to different concentrations of hydroxyethyl methacrylate (HEMA). The TNF- α secretion shown on the y-axis is plotted against the HEMA concentration on the x-axis for cells that were either stimulated by lipopolysaccharide (+LPS) or not stimulated by lipopolysaccharide (-LPS). HEMA reduces the immune response toward LPS/bacteria. (Courtesy Dr. John Wataha.)

thereby contributing to the potential immunotoxicity of some dental materials.

Effect on the Environment

Dental practice generates not only sharps and infectious waste but also chemical waste. In many countries the disposal of special chemical waste is regulated by laws. For example, any residues from placing amalgam fillings, such as scraps or used amalgam capsules, have to be disposed of properly. Of special importance are amalgam particles produced during the removal of amalgam restorations. So-called *amalgam separators* have been developed in order to remove—according to ISO 11143—at least 95% of these particles from the effluent water of dental practices. Within the Minamata Convention of 2013, aimed at reducing the discharge of mercury into the environment worldwide, the installation of such amalgam separators has been mentioned as one provision to reduce the mercury discharge from dental practices. Such particles are also generated during the removal of other restorative materials, such as resin composites.

CRITICAL QUESTIONS

What are the obligations of the clinician to prevent occupational hazards for the practice team?

Occupational Hazards for Dental Personnel

Dental technicians are exposed to significantly more metallic elements and monomers than the general population. Inhalation and aspiration of various dust and toxic vapors, which are generated during the heating, melting, and finishing of certain alloys and the processing of resin materials, may irritate the respiratory and gastrointestinal systems of these technicians and may cause toxic or allergic reactions.

Pneumoconiosis is a severe fibrotic lung disease that can be caused by chronic exposure to inorganic dust. A 1993 epidemiological study reported a prevalence of this lung disease in approximately 15% of dental technicians after 20 years or more of exposure. The prevalence in the general population is less than 1%. Pneumoconiosis is caused by dust that is generated during the finishing of base-metal frameworks and comprises silica and silicon carbide from abrasives ([Chapter 16, Biological Hazards of Abrasive Procedures](#)); asbestos; or alloys such as Co-Cr, Co-Cr-Mo, and Ni-Cr-Be. Silicosis is the most common occupational disease among dental technicians. According to the World Health Organization (WHO) International Agency for Research on Cancer (IARC), beryllium and beryllium compounds are carcinogenic to humans. The incidence of pneumoconiosis increases significantly among dental technicians working in laboratories with insufficient dust-handling facilities. However, such lung diseases may occur only if currently recognized safety precautions (see following discussion) are not followed. Furthermore, there is no evidence to suggest that metallic dental restorations increase carcinogenic risks in patients.

Dental technicians also report more allergic contact dermatitis than the general population because they have frequent contact with alloys or methacrylate-based monomers, such as methyl-methacrylate (MMA). However, data on the frequency of such reactions among dental technicians vary from slight to major risks. Improved safety measures in dental laboratories have reduced the frequency of contact dermatitis from allergen exposure, although wearing gloves may increase the allergic reaction to latex. The most frequent allergens are different acrylates, followed by metals like palladium and nickel.

Adverse occupational reactions are common for dental office personnel exhibiting various forms of hand or facial contact dermatitis, as well as respiratory disease. Contact-type reactions occurred most often because of exposure to acrylates, formaldehyde, fragrances, latex, and rubber additives. Allergic reactions to latex gloves are well recognized for dental office staff. Metallic dental materials do not seem to be a major occupational hazard for dental personnel. The special problems related to mercury handling are described later in the chapter (Dental Amalgam section).

Also, allergic respiratory problems such as asthma, rhinitis, and laryngitis have been reported for dental personnel, especially by dental auxiliary personnel. The reason is exposure to different acrylates, usually those contained in dental adhesives. If a type I reaction is suspected, a prick test (pricking the skin on the inner side of the forearm with a needle or pin containing a small amount of the allergen) can be performed.

Since the last century, dentists have worn gloves when treating patients, mainly to reduce the risk of microbial transmission. However, wearing gloves does not protect against the exposure of the skin to substances like monomers. Therefore a so-called “no-touch-technique” is recommended to avoid contact of uncured materials with both protected and unprotected skin.

Biocompatibility Testing

Biological testing of materials has evolved significantly since the 1950s and 1960s. Comparability of test results between laboratories was soon recognized to be possible only if test methods were standardized. In 1980 the Fédération Internationale Dentaire (FDI) published its “Recommended Standard Practices for Biological Evaluation of Dental Materials.” In the same year, American National Standards Institute (ANSI)/American Dental

Association (ADA) Specification No. 41, under the same title, became effective. Both documents were a collection of generally accepted standardized test methods and represented great progress toward the establishment of biological test programs for dental materials. The FDI recommendation has led to the publication of ISO 7405:1997, *Preclinical Evaluation of Biocompatibility of Medical Devices Used in Dentistry—Test Methods for Dental Materials*. This ISO standard was revised in 2008 and 2018. Meanwhile, ANSI/ADA No. 41 was also revised extensively and is now largely identical to ISO 7405:2018.

Purpose of Biocompatibility Testing

The primary purpose of biocompatibility testing is to protect dental patients, dental personnel, and the environment. Before the actual testing, there is a clinical risk assessment for the new material that needs to be completed. This risk assessment must take into consideration the intended function of the material in the mouth, the physical and chemical characteristics, the material’s release of substances, location, and the time of exposure. The outcome of the clinical risk assessment determines the tests to be performed.

The law requires that the manufacturer provides a clinical risk assessment together with necessary tests as a prerequisite for market access of new materials and for newly emerging risks for materials that are already on the market (see Legal Requirements section). The clinician should be familiar with the basic concepts of biocompatibility testing in order to be able to critically evaluate the claims of the manufacturers. As such, the discussion of the evaluation of biological effects of dental materials is based on the principles of (1) the release of substances to reach these sites, (2) their intrinsic (i.e., molecular) toxicity, (3) their concentrations, and (4) the exposure times, which may range from seconds to years. Finally, the relevant tests have to be performed and the risks fully evaluated.

CRITICAL QUESTION

How can a material exhibiting no obvious biological effects by itself alter body functions?

Release of Substances From Materials

Each biomaterial can degrade and release components under certain environmental and physical conditions. The environment–material interface is an active site for the corrosion of alloys that alters the material’s surface structure and releases metallic ions to the body. A decline in pH may also occur at the biofilm–material interface after intake of cariogenic food and may increase the corrosion of certain dental alloys and the release of substances from glass-ionomer cements (GICs). A change in the environment caused by acidic substances such as citrus juices or regurgitated hydrochloric acid can alter the surfaces of ceramics. On the other hand, high-pH environments may also increase the dissolution of some materials, such as glass-phase ceramics. Another factor that increases the potential for the release of substances is the surface roughness of a restoration or prosthesis. Rough surfaces promote the corrosion of alloys and the liberation of monomers and catalysts from resin materials.

Unfinished surfaces of resin composites and pit-and-fissure sealants have an oxygen-inhibited outer layer that may be more susceptible to leaching monomers or impurities such as bisphenol A.

Also, unpolymerized monomers or other unreacted components of set resin composites can be liberated over time. For resin-based composites, the lipophilicity of the environment is important, and more substances are eluted, for example, in ethanol compared with water. The release of substances generally declines after setting, as was shown for resin composites. However, substances are also released over an extended period of time.

Dose–Response Relationship of Toxicity

Paracelsus (1493–1541), who is sometimes referred to as the “father of toxicology,” stated, “All things are poison, and nothing is without poison; only the dose permits something not to be poisonous.” In short, “The dose makes the poison.” The statement indicates that toxicity is dose dependent; the effect of a specific dose of a therapeutic substance may be toxic, nontoxic, or beneficial. The quantity of a substance (in milligrams) ingested by test animals is often expressed as milligrams per kilograms of body weight (mg/kg bw).

Figure 17-15 shows a typical dose–response curve from a cell-culture test (**cytotoxicity test**), where cell viability, measured as relative optical density, decreases with an increase in the dose of the applied chemical (e.g., ZnCl_2). Two important concepts evolved from the dose–response plot. A dose can be described either as a lethal dose (LD), in which the response is the death of animals or cells, or an effective dose (ED), in which the response is another observable outcome. The plot allows us to identify the doses that affect a percentage of the exposed population. For example, **lethal dose fifty (LD_{50})** is the dose that kills 50% of the test organisms. The plot also shows that there are doses of a substance that do not elicit any adverse biological reaction, called the *threshold dosage*, and the highest nontoxic dose is the so-called **no-observed-adverse-effect level (NOAEL)**.

Not all biological reactions to dental materials follow this strict dose concept. As has been mentioned, allergic reactions can occur at much lower concentrations than toxic reactions, and they are rather insensitive to the concentration of allergen. Some even

claim that allergic reactions are dose independent. However, clinical experience shows that patients with proven contact dermatitis to nickel ions may, in certain cases, tolerate nickel-containing alloys in the mouth. One explanation is the extremely low concentration of Ni caused by the diluting effect of saliva.

CRITICAL QUESTION

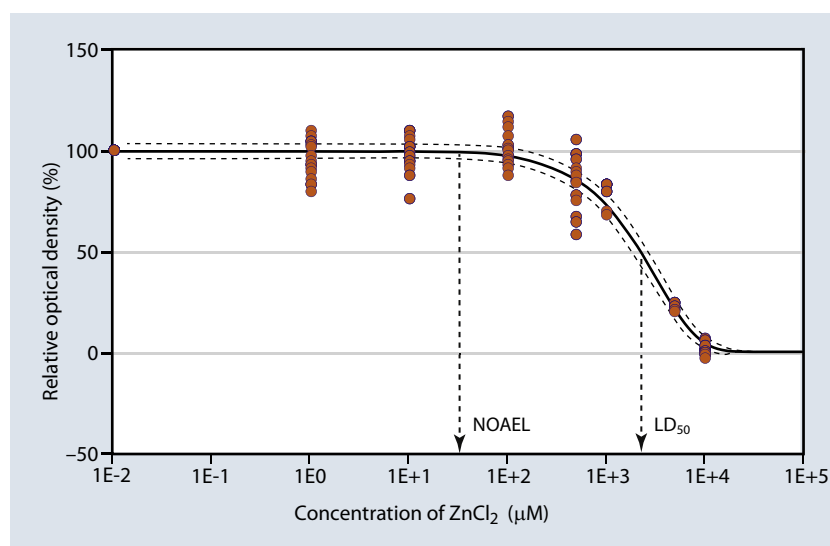
Why does test exposure time matter in conducting biocompatibility tests?

Test Requirements

The test conditions and the interpretation of the test results should reflect the nature of body contact and the duration of that contact (ISO 10993-1). The nature of contact can be a surface contact, an externally communicating medical device, or implanted medical devices. Materials may contact an intact or a breached surface. For instance, removable dentures contact the mucosal membrane, which mainly is intact, but periodontal dressings contact breached mucosal surfaces. Dental restorative materials generally belong to the group of externally communicating devices. This classification obviously reflects the presence or the lack of a barrier, such as the epithelium or the dentin, between the material and the target tissue. No such barrier is present for dental implants.

The duration of contact is grouped into (1) limited (≤ 24 hours), (2) prolonged (> 24 hours to 30 days), and (3) long term (> 30 days) contact (ISO 10993-1). For example, impression materials are used only for a few minutes, and temporary cements are in the mouth for up to a few weeks. For short-term exposures, the risk for allergic reactions is of special concern but not the risks of chronic toxic or mutagenic effects. In general, the most demanding tests are designed to evaluate materials that are expected to last for the longest times.

All available biocompatibility tests are so-called “models,” always representing one specific aspect of biocompatibility, and as such, a model may not meet all the requirements mentioned



• **Figure 17-15** Typical dose–response curve indicating the biological reaction (cell metabolism, measured as relative optical density) in relation to the applied dose of Zn^{2+} . Single measurements are shown (in circle) in combination with a best-fit curve (solid) and 95% confidence interval (dotted lines). The lethal dose fifty (LD_{50}) is the concentration of Zn^{2+} that affects 50% of the culture; the no-observed-adverse-effect level (NOAEL) is the highest concentration that has no effect.

previously. Therefore a set of tests is necessary for a final evaluation of the biocompatibility.

CRITICAL QUESTION

Is there one best test to measure biocompatibility?

Types of Biocompatibility Tests

Three types of tests are used to analyze the biocompatibility of dental materials: (1) *in vitro* tests, (2) animal tests, and (3) usage tests performed in experimental animals or humans. Tests can be performed either with the material or with an extract. Extracts are prepared by placing a test material with a defined surface into a liquid (e.g., saline or cell-culture medium) of a given volume for a defined period of time. The terms *eluate* and *extract* are often used synonymously in the literature.

In Vitro Tests

For *in vitro* tests, the candidate material or an extract of the material is placed in direct or indirect contact with some biological system outside of an organism in a container (e.g., cell-culture dishes or test tubes). Indirect contact involves a barrier such as agar, a membrane filter, or dentin between the test material and the target biological system. The goal of indirect contact is to improve the relevance of cell-culture tests for certain clinical situations. For example, a dentin–disk barrier mimics the tooth cavity in a cell-culture system. Biological systems may consist of mammalian cells, cellular organelles, tissues, bacteria, or certain enzymes. The main endpoints to be recorded are cytotoxicity, genotoxicity, and mutagenicity. *In vitro* tests are relatively fast and inexpensive. They can easily be standardized and controlled to provide highly reliable and reproducible measurements.

The *in vitro* tests, however, lack the ability to closely simulate the complex interactions that exist in an organism between and among the immune, inflammatory, and circulatory systems. The poor correlation between cytotoxicity assays and pulp reactions for some restorative materials in animal models has been reported. In conclusion, *in vitro* tests can be used to check if a substance eluted from the test material has the general potential to be harmful to cells. *In vitro* tests for assessing genotoxicity or mutagenicity are often used to assess the carcinogenic potential of a new material in order to avoid complex and expensive animal experiments.

Animal Tests

Animal tests differ from *in vitro* tests in that an intact animal (e.g., cats, ferrets, guinea pigs, hamsters, mice, and rats) is used rather than cells or tissues of animal or human origin. In some animal tests, the test materials are not applied as intended in dental patients (e.g., restorative materials are implanted subcutaneously in rats for evaluation of nonspecific toxic response). For acute or chronic toxicity tests to determine LD₅₀ values, test materials are ground and fed to animals. Because oral ingestion in such quantities is not realistic, the relevance of such tests for dental materials is questioned. Many other animal models are described in the literature for testing certain material properties (e.g., **carcinogenicity**), but they are rarely used for testing dental materials, and respective *in vitro* methods are used instead.

The advantage of animal tests lies in their ability to permit intact biological systems to respond to or interact with a candidate material. The disadvantages of animal tests are their high costs, the difficulty in controlling confounding factors, and the length of

time that may be required to obtain a measurable response. Also, animal rights activists and other individuals criticize these tests because of ethical concerns regarding the use of animals. Finally, the relevance of animal tests in simulating human responses is often challenged. In spite of these disadvantages, animal tests are still relevant for evaluating certain risks of new materials prior to their clinical use, such as testing the sensitization potential in guinea pigs.

Usage Test

In this group of tests, materials are applied in the test animal as they are in the patient (e.g., a class V cavity is prepared in monkey teeth and filled with the test material). After up to 3 months, the pulp reaction is evaluated histologically. Such usage tests can also be performed in humans (e.g., in teeth scheduled for extraction for orthodontic reasons). The choice of animals for a usage test usually involves larger animals with an anatomy similar to that of humans, such as dogs, monkeys, or sheep. The ultimate relevance of a usage test depends on the extent to which the test simulates the clinical use of the product.

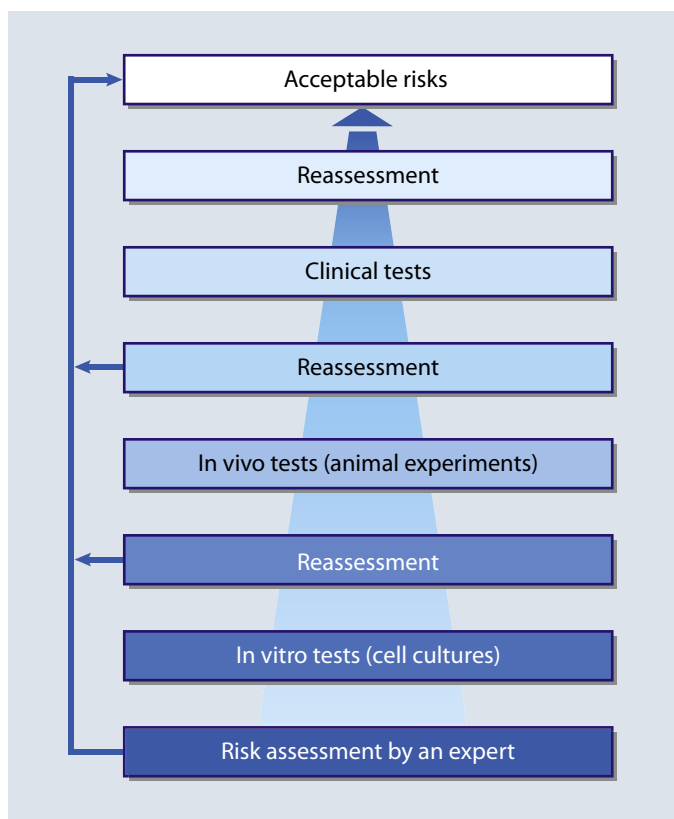
Human clinical trials may be regarded as the best-known usage test, but there are limitations. Very often no histology is performed, and from clinical symptoms alone, no evaluation of the real damage to the pulp after placement of a restorative material is possible. Furthermore, teeth scheduled for extraction because of orthodontic reasons are normally obtained from young patients. These teeth have rather open apices, which may react differently from the teeth of older patients, which have narrow apical openings and may potentially have previous pulp damage from caries.

Usage tests involving either animals or human subjects have several disadvantages, including their design complexity, the difficulty in controlling experimental variables, and interpretation challenges. If humans are used in a clinical trial, approval for the proposed usage tests must be obtained from an institutional review board. Such tests usually take a long time, which adds considerably to the typically high cost of using human subjects. Finally, human usage tests may involve legal and confidentiality issues that do not occur for animal and *in vitro* tests.

All test methods just mentioned have advantages and limitations. As cell-culture techniques evolve, animal-based tests are continuously being replaced by *in vitro* tests, along with imaging techniques and research focused on mechanisms that control the biological responses to materials. Biocompatibility testing in the future may lead to more reliable predictions of adverse effects, and this knowledge of biological properties may allow us to formulate materials that provide specific, desired biological responses. However, one should keep in mind that to date, no test can guarantee that a substance will not cause an adverse effect in individuals exposed to that material in the clinic. Therefore postmarket surveillance is of utmost importance (see Legal Regulations and Risk Classes section).

Test Strategy

All test methods discussed previously have obvious pros and cons, and thus following certain test strategies is advisable. *In vitro* tests should initially be performed for cytotoxicity or genotoxicity/mutagenicity evaluation. Assessment is then made if the results from *in vitro* tests together with what is known from the literature are sufficient to fulfill the biocompatibility criteria. If not, animal tests such as allergy tests using guinea pigs are performed. Afterward, a new assessment is made to determine whether further testing is necessary. The strategy is shown in Figure 17-16. Clinical tests in some



• **Figure 17-16** Strategy of biocompatibility testing. Based on a clinical risk assessment if necessary, in vitro tests are performed. After reevaluation, it will be decided if an animal test is necessary. Then a further reevaluation follows, and so forth. (From Schmalz G, Arenholt-Bindslev D, editors: *Biocompatibility of Dental Materials*. Berlin-Heidelberg, 2009, Springer.)

countries are mandatory for materials that are considered to be of high risk. The final decision for market clearance is then made by an interchange between manufacturers and a government agency (e.g., the U.S. Food and Drug Administration [FDA] in the United States) or a private organization with authority granted by a government agency.

CRITICAL QUESTION

If you were presented with a new material, never before used in a human being, how would you decide if it was safe for use as a dental restorative material?

Responsibilities

The manufacturer is responsible and liable for a new material to meet all requirements regarding biocompatibility (see Legal Regulations and Risk Classes section). When such products are released to the profession, dentists, dental staff, and patients must assume that sufficient safety testing has been performed to minimize potential risks. The question is, how much evidence is sufficient to demonstrate that a product is sufficiently safe for general clinical use? The consensus of several parties (i.e., manufacturers and government agencies) is a prerequisite, as discussed later in this chapter. In addition, the clinician also has certain responsibilities in this respect.

First of all, the clinician must strictly follow the instructions for use with the correct material indications. If the clinician does

not follow the indication, the manufacturer is no longer liable. Furthermore, the clinician must apply state-of-the-art techniques; for instance, insufficient curing of resin materials results in increased cytotoxicity of the material and impaired mechanical properties.

New risks may arise with materials already on the market (e.g., estrogenicity associated with sealants), and the clinician must be able to critically assess the information provided by the manufacturer or in the scientific literature. The information on biocompatibility provided by the manufacturer may be insufficient because the detailed composition of the materials is often not declared. If a patient is allergic to certain monomers or metals, the clinician needs to know the composition of the material to be used to avoid an adverse effect. If in doubt, the clinician can contact the company directly to obtain this information.

Manufacturers often make special claims regarding their materials, such as bioactivity. The clinician must be very critical of such claims, which should only be generated on the basis of neutral information and basic knowledge. More importantly, one can search for the most current evidence in the PubMed, Web of Science, or other databases with key words or MeSH terms.

A request should be made to national agencies in the dentist's home country to determine whether any adverse-event reports have been made. As one might expect, unless catastrophic failures have occurred soon after the product's introduction, the shorter the time that the product has been in existence, the smaller the number of adverse-effects reports that will be found. Furthermore, legal regulations may require that dentists report adverse reactions they observed with their patients (see Postmarket Surveillance section).

Finally, the clinician should be well informed about the biocompatibility of dental materials to answer the queries of patients. Biocompatibility is a current topic for the media, and there is lots of information available on the Internet, some of which is not based on scientific evidence. The clinician must be able to provide correct answers to the patient.

Biocompatibility Testing Standards

Because of the multifactorial nature of biocompatibility and the large number of different test methods described in the literature, standardization is essential for the unbiased comparison of results from different studies, and standards are helpful to fulfill the legal requirements for biocompatibility. The two ISO standards relevant to the biocompatibility of devices and materials in dentistry are ISO 10993, Biological Evaluation of Medical Devices; and ISO 7405:2018, Evaluation of Biocompatibility of Medical Devices Used in Dentistry.

ISO 10993 consists of more than 20 single standards and related documents, each addressing a different area of biological testing of medical devices (which includes dental materials). For example, Part 1 describes the general requirements for biocompatibility testing; Part 3 describes tests for genotoxicity, carcinogenicity, and reproductive toxicity; Part 5 describes different tests for cytotoxicity; and Part 10 describes tests for irritation and skin sensitization. ISO 7405:2018 describes the tests that are specific to dental materials. For example, the standard describes dentistry-specific cytotoxicity tests and all usage tests, such as the pulp/dentin test, the pulp capping test, the endodontic usage test, and the implant usage test, as well as the dentin-disk barrier test in a cell-culture system described earlier. Clinical risk assessment (see Figure 17-16) can be performed as recommended in ISO 14971:2019, Medical Devices—Application of

Risk Management to Medical Devices, where the different steps for selecting the appropriate tests are delineated.

Standards are regularly reviewed and revised. However, standards also have some disadvantages. Standards may not always keep pace with the development of new scientific technology. In addition, standards are developed based on agreements and compromises among manufacturers, academicians, and the dental profession, which is a time-consuming process. Standards may be considered arbitrary in nature because certain tests are selected out of a larger number of methods. However, in spite of these limitations, standards for biological testing are necessary to ensure the biological safety of medical and dental products, and they are generally considered to represent the state of the art in biocompatibility testing.

Safety Data Sheets

Each dental product is supplied with a Safety Data Sheet (SDS), also known as a *Material Safety Data Sheet (MSDS)* before 2013 or a *product safety data sheet (PSDS)*. In the United Kingdom, the Control of Substances Hazardous to Health (COSHH) requires such information. This is a standardized report on the properties of a particular product/substance, for example, melting point, boiling point, and flash point. This report is intended for occupational settings and is essential for users and emergency personnel because this data sheet describes procedures for handling or working with the material safely. In addition to physical data, this document identifies toxicity risks, health effects, first-aid procedures, reactivity, storage and disposal conditions, and where applicable, procedures for fire-fighting. Furthermore, SDSs contain information on the types of protective equipment that should be used and procedures that must be followed for accidental releases and handling of spills. Limited information on the composition of the material is also included.

Labeling

Labeling requirements are based on national or international legislation. Besides other obligations, potentially harmful substances must be properly labeled to minimize the risk of injuries to anyone who may come in contact with them and the risks of environmental exposure. The United Nations has installed a Globally Harmonized System of Classification and Labeling of Chemicals (GHS), which provides a harmonized basis for labeling. Special pictograms may be placed on the package in addition to so-called *H- and P-statements*. H-statements are a set of standardized phrases about the hazards of chemical substances. P-statements are a set of precautionary statements. Examples of the GHS pictograms are shown in Figure 17-17.

Legal Regulations and Risk Classes

The Dental Products Panel (DPP) of the FDA Medical Devices Advisory Committee reviews and evaluates data concerning the safety and effectiveness of marketed and investigational products for use in dentistry, endodontics, or bone physiology relative to the oral and maxillofacial area and makes appropriate recommendations to the Commissioner of Food and Drugs.

Risk Classes

The FDA classifies all medical devices into one of three classes—Class I, II, or III—according to the risk-based regulatory

controls necessary to provide a reasonable assurance of the safety and effectiveness of a device. Class I devices generally pose the lowest risk to the patient/user, and Class III devices pose the highest risk. Dental devices that are not specifically exempted are required to be cleared by FDA prior to distribution into interstate commerce.

There are three levels of regulatory controls: general controls, special controls, and premarket approval (PMA). General controls have the least amount of regulatory control and are used whenever the level of device risk is low. They apply to all three classes of devices and include adulteration or misbranding, device electronic establishment registration and listing, premarket notification, quality systems, medical device reporting, and labeling. Special controls apply when general controls alone are insufficient to ensure safety and effectiveness. They apply to Class II devices and include device guidelines and manuals, adhering to mandatory performance standards, recommendations or other actions, and special labeling. PMA is necessary whenever general or special controls cannot provide sufficient information to ensure medical device safety and effectiveness. They apply to Class III devices and include clinical investigations, safety and effectiveness data, adverse reactions and complications, patient information, and many more according to the type of device.

If the manufacturers intend to introduce a device to the U.S. market that does not require the standard PMA (e.g., Class II devices), they need to submit a 510(k). The 510(k) is a premarket submission to FDA to demonstrate that the device is at least as safe and effective as, that is, substantially equivalent to, a legally marketed device that is not subject to PMA. Most of the submissions to the Dental Branch are 510(k) types of submissions.









Similar regulatory systems have been established in other parts of the world. For example, the EU system also uses risk Classes I, II, and III but subdivides Class II into IIa and IIb. Dental devices are mainly in Class I or IIa; dental implants are in Class IIb. Class II devices require the involvement of a “notified body,” and Class III require a device examination by a “notified body” (comparable to the PMA).

Postmarket Surveillance

Even if all available test methods and required evidence are used and exercised with due diligence, an adverse reaction may still occur when a large population is exposed to a new material. Therefore clinicians are required (in some countries by law) to report observed adverse reactions to competent authorities. The FDA receives adverse-event reports on devices as either individual reports or summary reports. Individual reports include voluntary reports submitted by health care providers and consumers through MedWatch (<http://www.fda.gov/Safety/MedWatch/default.htm>), the safety information and adverse-event reporting program of the FDA. Manufacturers and user facilities submit mandatory reports.

Side Effect of Various Material Groups

To assess the biocompatibility of a material, it is necessary to know the composition, the substances released, and the chemical/physical characteristics of both the material and the substances released. Biocompatibility cannot be predicted by the composition alone. The material groups of interest include dental amalgam, methacrylate-based resins, dental alloys, dental ceramics, hydrofluoric acid, GICs, and latex products.

PICTOGRAM	MEANING OF PICTOGRAM	TYPE OF HAZARD(S) (Associated with this pictogram)
Health Hazard 	The chemical is a risk to health if used improperly.	<ul style="list-style-type: none"> • Carcinogen • Mutagenicity • Reproductive Toxicity • Respiratory Sensitizer • Target Organ Toxicity • Aspiration Toxicity
Severe Toxic 	The chemical is a serious health or physical hazard or poison. It will produce adverse effects following a single dose. This pictogram is usually used in combination with the Health Hazard Pictogram.	<ul style="list-style-type: none"> • Acute Toxicity (fatal or toxic) if inhaled or swallowed, or if it comes in contact with the skin.
Acute Toxic 	The chemical may cause immediate, serious health effects but it is less severe than the Severe Toxic pictogram (skull and crossbones). This pictogram is usually used in combination with the Health Hazard Pictogram.	<ul style="list-style-type: none"> • Irritant (skin and eye) • Skin Sensitizer • Acute Toxicity • Narcotic Effects • Respiratory Tract Irritant
Flammable 	The chemical may burst into flame. Be careful to keep away from ignition sources and combustible materials.	<ul style="list-style-type: none"> • Flammables • Pyrophorics • Self-Heating • Emits Flammable Gas • Self-Reactive • Organic Peroxides
Corrosive 	The chemical is a physical or health hazard that can easily damage skin or eyes. Be aware of PPE and storage requirements.	<ul style="list-style-type: none"> • Skin Corrosion/Burns • Eye Damage • Corrosive to Metals
Oxidizer 	The chemical may cause other materials to ignite or burn faster. It can create an increased fire risk in work or storage environment.	<ul style="list-style-type: none"> • Oxidizers
Gas Under Pressure 	This chemical consists of pressurized gas that would explode, rocket, or damage health if heated, ruptured, or leaking.	<ul style="list-style-type: none"> • Gases Under Pressure
Explosive 	This material can blow up or otherwise create an uncontrolled reaction. Should be treated with extreme caution.	<ul style="list-style-type: none"> • Explosives • Self-Reactives • Organic Peroxides

• **Figure 17-17** Examples for labeling according to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) system. This labeling system, developed for chemicals, is often used for labeling dental materials.

CRITICAL QUESTION

What evidence or documentation can you provide to dental patients to assure them that amalgam is a safe material for dental restorations for the general population?

Dental Amalgam

Although amalgam is an alloy of metals such as Ag, Sn, Cu, or Zn with Hg, most of the controversy stems from the known toxicity of mercury and the question of the toxic effects of mercury within amalgam restorations.

Mercury

Mercury occurs naturally and exists in the environment in three forms: metallic mercury (Hg^0), inorganic salts (HgS and HgCl_2), and organic mercury (CH_3Hg and $\text{C}_2\text{H}_5\text{Hg}$). Microorganisms and various natural processes can convert metallic mercury to inorganic compounds, inorganic mercury to organic compounds, or organic mercury to inorganic compounds. Methylmercury is the most common organic form that is transformed by natural processes in the environment and is more toxic than ethyl mercury, metallic mercury, or the inorganic salts. Methylmercury is a major safety concern because it bioaccumulates through the food chain, mainly in large fishes such as sharks, swordfish, and tuna, and enters the human body through fish consumption. Metallic mercury accumulates in the kidneys and the brain. In the brain, metallic mercury can be converted to inorganic salt with an increased retention time. The half-life ranges from 13 to 99 days depending on the form, with metallic mercury exhibiting a longer half-life than inorganic forms. Evidence from primate studies, human case studies, modeling studies, or experimental studies shows a large variation of data, but the half-life of inorganic mercury in the brain may be years or decades.

Metallic mercury gains access to the body via the skin or as a vapor inhaled through the lungs. Ingested metallic mercury is poorly absorbed from the gut (0.01%), which makes inhalation of mercury vapor the primary portal into the body. Absorption of ingested inorganic mercury in the gut is 1% to 7%. Excretion may occur through exhaled vapor or through urine, feces, or skin (sweat). For example, mercury vapor is readily absorbed after inhalation. Dissolved mercury can be transported through blood and distributed to the brain and other organs and excreted by exhalation and in urine. Metallic mercury is transported to blood cells and tissues, where metallic mercury is oxidized rapidly to mercuric ions (Hg^{2+}).

Numerous tests for the body burden of mercury have been developed, including those based on the analysis of blood, urine, and hair. Of these test parameters, the measurement of mercury in the urine after 24 hours may be the best long-term indicator of the total metallic mercury body burden (expressed as $\mu\text{g/L}$) or normalized to grams of creatinine in urine (expressed as $\mu\text{g/g}$ creatinine). Normal levels of creatinine in urine are between 0.6 and 1.1 mg/dL (females) and 0.7 and 1.3 mg/dL (males). Sampling of metals in hair, nails, feces, bone, and teeth is also advocated in certain cases as a partial indication of long-term exposure.

Symptoms of Mercury Poisoning

The nervous system is sensitive to all forms of mercury, although the brain is most sensitive to metallic mercury and methylmercury. Acute symptoms of mercury poisoning are mainly a result of

spillage of liquid mercury in confined industrial spaces. The first sign is dyspnea. This may be followed by paroxysmal cough, chest pain, pulmonary infiltration, chills, nausea, and vomiting. Fatal outcomes have also occurred.

Chronic exposure levels indicated by a mercury concentration in urine of 5 $\mu\text{g/g}$ creatinine (or 7 $\mu\text{g/L}$) are associated with no risk; concentrations of >20 $\mu\text{g/g}$ creatinine are associated with increased risk of subtle or unclear symptoms; at 50 $\mu\text{g/g}$ creatinine, subclinical adverse effects of kidney function may occur; and the level of 100 $\mu\text{g/g}$ creatinine is considered the onset of mercurialism. Symptoms of mercurialism include weakness, fatigue, anorexia, weight loss, insomnia, irritability, changes in personality, dizziness, tremors in the extremities or the eyelids, memory loss, and impairment of vision and hearing. Although amalgams do not release anywhere near toxic levels of mercury, the long half-life of mercury in the body raises concerns among some individuals.

Mercury Release From Amalgam and Body Uptake

A low quantity of mercury is released from amalgam restorations as a result of a passive tarnish layer on the surface. The total mercury uptake from dental amalgams was estimated to be 1 to 3 $\mu\text{g/day}$, depending on the number and size of amalgam restorations present, although an uptake as high as 17 $\mu\text{g/day}$ has been reported. The WHO limit for the provisional tolerable weekly intake (PTWI) value is 5 $\mu\text{g/kg}$ bw or 50 $\mu\text{g/day}$ for a 70-kg person. The main source of mercury uptake from amalgam fillings is inhaled mercury vapor. Methylmercury is not released from amalgams but is generally a product of bacteria or other biological systems acting on metallic mercury, mainly in the environment and taken up by humans through fish consumption. The conversion of inorganic mercury into methylmercury inside the human body generally does not take place or only in minor amounts. The total uptake of mercury from amalgam fillings is reflected in an increased blood/urine level of mercury. An increase of 1 to 1.8 $\mu\text{g/L}$ of mercury in urine for each 10 restored amalgam surfaces is estimated, with more recent data demonstrating lower values.

Levels of 1 to 5 $\mu\text{g/L}$ in urine were described as the normal range for nonoccupational groups. A 2013 study by Nicolae et al. reported that 5418 Canadians, aged between 6 and 79 years, with amalgam restorations of up to 65 surfaces per individual showed that the mean urine mercury concentrations for 98% of the group were below the levels associated with any health risks. One study estimated the uptake of food-related organic mercury to be approximately six times greater than the uptake of mercury from amalgam restorations. A large survey of the U.S. population published in 2016 confirmed that the inorganic mercury concentration in the blood increases with the number of amalgam restoration surfaces. However, the level was well below the safety threshold established by the WHO and the Environmental Protection Agency (EPA).

The mercury burden of dental personnel is usually higher than for patients because of the application or removal of amalgam fillings but has decreased in recent years, probably as a result of improved handling techniques with amalgam, such as the use of amalgam capsules.

Clinical Symptoms After Amalgam Application

Most claims for adverse reactions to amalgam have been related to systemic effects. A main concern was directed toward the problem of neurological effects of mercury from amalgam fillings in children.

Systemic Reactions

Two extensive studies, the [Casa Pia study](#) of Portugal led by Dr. Timothy DeRouen and the [New England study](#) of the United States led by Dr. David Bellinger, were performed in parallel and reported in 2006. Each study included more than 500 children divided into two groups; one group received amalgam, and the other group received resin composite fillings. After 5 years, the level of mercury in urine in the children was larger with the amalgam group than that in the resin composite group in both studies. However, no neurological effects could be observed with either group in both studies. Later, the data/material of the studies was used for further biochemical analyses or genetic testing, and new groups of the children were formed. However, the results had been inconsistent, and such “post hoc” analyses (regrouping of existing data sets) are regarded as precarious because of possible bias.

The literature on the possible adverse effects of mercury from amalgam is very extensive. The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR), a scientific commission of the EU, published a review in 2015 of recent existing literature, which concluded that the current evidence does not preclude the use of amalgam for the general population. However, the choice of material should be based on the medical history of the patient, such as allergies or severe renal diseases, which impair the renal excretion of mercury. In summary, there are no data to show that mercury released from dental amalgam is harmful to the general population. The observation has been confirmed by a 2020 literature survey from the International Association for Dental Research (IADR) Science Information Committee.

Nevertheless, a small number of patients claim that their complaints/symptoms are derived from their amalgam fillings. Several studies have investigated if claimed symptoms had disappeared after the removal of amalgam. [Nerdrum et al. \(2004\)](#) could not find any significant improvement of the symptoms after 7 years, but a questionnaire-based study by [Kristoffersen et al. \(2016\)](#) revealed some improvement. [Melchart et al. \(2008\)](#) reported that implementing a health-promotion program aimed at developing health-related lifestyle management skills had a similar effect as amalgam removal on the reduction of subjective complaints. The study also reported a significant reduction of the inorganic mercury concentration in the blood and urine for the amalgam-removal group.

Local Reactions

Lichenoid reactions have been associated with contact allergy to mercury from amalgam restorations and possibly mechanical irritation by the restoration. Their appearance can be whitish plaque-like

or even with erosive parts. In the presence of such a reaction, the amalgam restoration should be corrected to remove the mechanical irritant or replaced with a mercury-free material. A study of patients with oral lichenoid contact reactions and positive patch-test reactions to mercury compounds showed that partial or complete replacement of amalgam fillings led to a significant improvement in nearly all patients. In very rare cases, a carcinoma may develop following a localized lichenoid reaction. These patients should be monitored regularly and referred to a specialist if the reaction persists.

Amalgam debris can be trapped in the mucosal connective tissue during placement or removal of amalgam restorations through mucosal abrasions, lacerations, or compaction into the gingival sulcus. Amalgam may enter the socket or periosteum during tooth extraction or be left within the surgical site of an endodontic retrofill procedure. Over time, the debris corrodes and causes discoloration of the mucosa, known as an *amalgam tattoo* ([Figure 17-18](#)). Implanted amalgam does not normally cause acute tissue reactions and is normally totally asymptomatic. Therefore these fragments of amalgam generally do not need to be removed except for diagnostic reasons.

Allergic Reactions

Allergic reactions have been described, mainly related to mercury but less to amalgam. If a patch test of mercury is positive, no new amalgam restoration should be placed. Existing amalgam restorations should be replaced, if clinical symptoms are present.

FDA Recommendations

Recently, FDA has issued new recommendations for the use of dental amalgam (<https://www.fda.gov/medical-devices/dental-devices/dental-amalgam-fillings>). Briefly, FDA states that the majority of evidence suggests exposure to mercury from dental amalgam does not lead to negative health effects in the general population. Exposure to mercury may pose a greater health risk in certain groups of people, who may be more susceptible to potential adverse effects generally associated with mercury. These high-risk populations include:

- Pregnant women and their developing fetuses
- Women who are planning to become pregnant
- Nursing women and their newborns and infants
- Children, especially those younger than six years of age
- People with pre-existing neurological disease
- People with impaired kidney function
- People with known heightened sensitivity (allergy) to mercury or other components of dental amalgam



• **Figure 17-18** Large blue-colored areas, typically referred to as an *amalgam tattoo*, which is a benign area of discolored mucous membrane in the mouth. These examples are not associated with allergic reactions to mercury or any other metallic elements in the amalgam fillings. The discoloration is caused by small amalgam granules that have fallen into open wounds created during the condensation and carving of amalgam fillings in prepared teeth (**A** and **B**) or retrograde fillings in root apices (**C**). (Upper two photos, Courtesy Dr. Hyun-Ju Chung.)

The FDA strongly encourages that alternative, non-mercury materials such as resin composites or glass ionomer cements be used when possible and appropriate. In addition, The FDA does not recommend anyone remove or replace existing amalgam fillings in good condition unless it is considered medically necessary by a health care professional.

Environment

In 2013, the Minamata Convention was signed and ratified by more than 120 countries, where participating countries are legally bound to reduce the mercury burden to the environment. Although the relative contribution of dental amalgam to environmental mercury exposure compared with fossil fuel combustion or small business gold mining is very low, a phase-down of dental amalgam use was agreed upon. A number of provisions for such a phase-down have been listed in the Minamata Convention of 2013; provisions include improved caries prevention, the use of amalgam capsules, the installation of amalgam separators, and the research/development of new alternative materials. The clinician should check with the local authorities for the respective legal regulations to follow with regard to amalgam waste disposal.

Handling of Mercury in the Dental Office

Because of the potential health risks for dental personnel exposed to mercury from handling amalgam, special care must be exercised when using dental amalgam. In 2003 the ADA issued detailed recommendations that ensure safe handling of amalgam and amalgam waste. For more details, see [Chapter 8, Mercury Hygiene in Dental Offices](#).

Methacrylates and Resin Composites

There is ample evidence that dental adhesives and resin materials release free monomers into biological environments over extended periods of time. Additionally, catalysts, accelerators, other additives, components within filler particles, and nanoparticles can be liberated. The amount of released substances depends on the degree of polymerization. Undercuring leads to an increased amount of released substances and increased cytotoxicity. Monomers have been shown to evaporate during procedures in the dental offices or processing in the dental laboratory. The measured monomer concentrations in the dental office are well below limit values but greater in the dental laboratories despite mandatory specific safety precautions. Although noticeable nanoparticles are released during grinding, polishing, or restoration removal, the amount of released particles is low, and no health risk for the dental personnel and the patient can be assumed. The main interest of this section is directed to the monomers that include *bis*-GMA and related molecules, urethane dimethacrylate (UDMA), TEGDMA, HEMA, or bisphenol A dimethacrylate (*bis*-DMA). Polyacid modified resin composites (“compomers”) have a similar composition as resin composites, and they can be assumed to have the same biological properties.

CRITICAL QUESTION

Why can resin composites be used although bisphenol A is released?

Systemic Reactions

Presently, the most intensively discussed systemic effect of resin materials is the (claimed) estrogenicity of bisphenol A (BPA) released from dental resin materials. The evidence of BPA estrogenicity is

derived from molecular modeling studies and in vitro studies of estrogen receptor–BPA binding. These studies also show that BPA is probably 1000-fold less potent than the native estrogen hormone. Nonetheless, a number of diseases have been claimed to be associated with BPA exposure from many environmental sources, such as food can linings or polycarbonate plastics.

BPA is a precursor of *bis*-GMA, *bis*-DMA, and similar aromatic monomers, which are used in resin composites. BPA can exist as an impurity in both monomers. *Bis*-GMA under physiological hydrolytic conditions does not degrade into BPA, but *bis*-DMA does. BPA is released from resin composites made of *bis*-GMA or related monomers over time as a result of the aforementioned impurities and from *bis*-DMA materials, also as a result of degradation. However, the total release is very low and several orders of magnitude below the presently accepted toxicological limit value for systemic exposure of 4 µg/kg bw.

In vitro studies by [Schweikl et al. \(2006\)](#) showed that monomers such as HEMA or TEGDMA are genotoxic and mutagenic. These effects could be related to an intracellular increase of ROS, which occurred after GSH depletion resulting from monomer detoxification. As a result of a functioning p-53 protein, DNA damage was either repaired or the cells were transferred to apoptosis. Thus no tumor formation has been reported as a result of resin composites.

As discussed before, nanoparticles are generated during grinding, polishing, or removal of resin composites restorations, but the quantity is so small that no risk can be assumed for the dental personnel and the patients. Nonetheless, the FDI issued recommendations in 2018 for dental personnel to further reduce the risk. They should use ample water spray during procedures whenever possible, wear a surgical mask, and sculpt restorations to near-desired form before light curing, thus reducing dust generation.

Local Reactions

Pulp Reactions

Postoperative discomfort/sensitivity or pain shortly after the placement of resin composite restorations has often been attributed to fluid movement in the dentinal tubules but not to toxicity, even though resins before polymerization are known to be cytotoxic in vitro and leachable components traverse dentin. However, no toxic reaction of the dental pulp is observed histologically if the remaining dentin thickness is well above 0.5 mm. For deep cavity preparations, the observations are inconsistent, with some reporting no pulp reaction, mainly in animal experiments, and others reporting such reactions.

In a direct pulp capping situation, pulpal inflammation with or without a dentin bridge (reparative dentin) has been described in patients. Interestingly, some studies using monkey models showed that resin materials did not cause an inflammation, and dentin bridging occurred. On the other hand, Bergenholtz, in 2000, reported an association of pulpal inflammation under resin composite restorations with the presence of bacteria at the cavity floor. The clinical consequences are that in flat or medium cavities, the meticulous use of adhesive technique is most important in order to avoid any bacteria at the cavity floor, and there is no risk of chemical pulp damage by the resin materials. Incorporating an antibacterial monomer in the adhesive resin has been reported. However, in deep cavities with the potential for pulp exposure, a base (e.g., a tricalcium silicate cement) should be applied at the cavity floor close to the pulp.

The use of high-irradiance light-curing units (LCUs) may also lead to pulp damage in deep cavities. LCUs with no more than

2000 mW/cm² and exposure times of up to 20 sec are generally used in dental practice. If LCUs with >2000 mW/cm² even with shorter exposure times are recommended, the manufacturer must provide sound scientific evidence of no tissue damage.

Gingival Reactions

Gingivitis close to resin-based composite fillings is mainly related to the property of resin materials facilitating biofilm formation. The acidic monomers in adhesives may cause a chemical burn on the gingiva, which heals within a few days. Denture stomatitis may appear as small reddish areas (Figure 17-10, A) on the mucosa covered by an acrylic-based appliance. Undercuring results in an increased release of cytotoxic monomers, with possible toxic effects on the adjacent gingiva in deep approximal cavities. An LCU with a very high irradiance may lead to local burns of the lips and the tongue, and a rubber dam provides no protection.

Allergic Reactions

Nearly 2% of dental personnel have been described to be allergic to resin-based adhesives/composites because of frequent exposure to nonpolymerized materials. The allergenicity of methacrylate-based materials such as HEMA or TEGDMA is well documented, and the use of gloves is not effective in preventing contact because most monomers diffuse easily through gloves, especially when diluted with organic solvents, as in many dental adhesives. One study showed that the best substance for screening allergies to methacrylate-based products is HEMA, which confirmed 96.7% of the dental patients with a suspected methacrylate allergy and 100% of the dental personnel with clinical symptoms of a methacrylate allergy.

The allergic reactions occur primarily as contact dermatitis, with the resins acting as haptens via delayed hypersensitivity (type IV) mechanisms. In rare cases, anaphylactic responses have been reported, with asthmatic symptoms, severe urticaria, and skin rashes and swellings on the entire body, followed by the formation of blisters on the child's face, ears, and lips. In rare cases, allergic rhinitis or other reactions of the respiratory tract have been described. Cross-reactivity between different monomers has been observed.

Dental Alloys

As discussed in Chapter 9, Alloy Classification by Principal Elements, dental alloys usually contain multiple elements and are commonly described by their major components. The microstructure of alloys may be classified as single phase (solid solution) or multiple phases depending on the difference in the atomic structure between elements (Chapter 2, Equilibrium-Phase Diagrams). The composition and the phase structure significantly influence the release of substances in the oral environment. This section will discuss the release mechanism and biological effects of alloys and the allergy reactions of some common elements used in dental alloys.

CRITICAL QUESTION

How does the corrosion of metals contribute to their biocompatibility?

Metal Ions Released From Alloys

Dental casting alloys are made corrosion resistant through the use of noble metals (e.g., high-noble and noble alloys) or the use of chromium and titanium to form a protective passivation layer on base-metal and titanium alloys (Chapter 9, Predominantly Base-Metal Alloys). However, some elements in the alloy lose electrons and become cations as they are released in the oral cavity.

Normally, dental alloys can release sufficient metal ions to cause adverse effects in some cases but not enough to alter the esthetic appearance or cause failure of the prostheses.

Several statements can be made about the release of elements from dental casting alloys. First, multiphase structures often increase the elemental release from alloys. Second, certain elements have an inherently higher tendency to be released from dental alloys, regardless of alloy composition. In other words, the release of metal ions from the alloys is not necessarily proportional to the nominal alloy composition. Third, microscopic particles can be abraded from metallic restorations during wear processes that accelerate the corrosion processes in vivo because of the loss of the passivation layer. Fourth, certain environmental conditions around the alloy, such as a decline in pH under a biofilm, will affect the release of elements. For in vitro studies, the chemical composition and characteristics of the cell-culture medium, pH, ion composition, and serum are significant variables that dictate the environment. For in vivo conditions, the biological factors that may contribute to alloy corrosion include the biofilm, organic acids, types of enzymes produced by oral microorganisms or those present in food, and phagocytotic cells such as human neutrophils. There are also interaction factors between alloys and the patient, such as the consumption frequency of acidic foods and beverages and the composition of saliva.

On the basis of these studies, the release of metal ions cannot be clearly predicted from the nobility or the overall composition of cast alloys. Each product must be evaluated individually for its corrosion behavior and the release of metal ions in specific corrosive environments.

Systemic Reactions

Genotoxic effects have been reported for beryllium and gallium salts. Alteration of DNA repair processes and carcinogenic effects have been reported for Cd²⁺, Ni²⁺, and Co²⁺. There is some evidence suggesting that nickel, cobalt, and chromium tend to increase cancer risk in humans. Beryllium is a documented carcinogen. Although the release of beryllium from alloys containing beryllium and of Ni²⁺ and Co²⁺ from respective alloys has been documented intraorally and in vitro, there are no studies showing that these dental alloys cause cancer in patients.

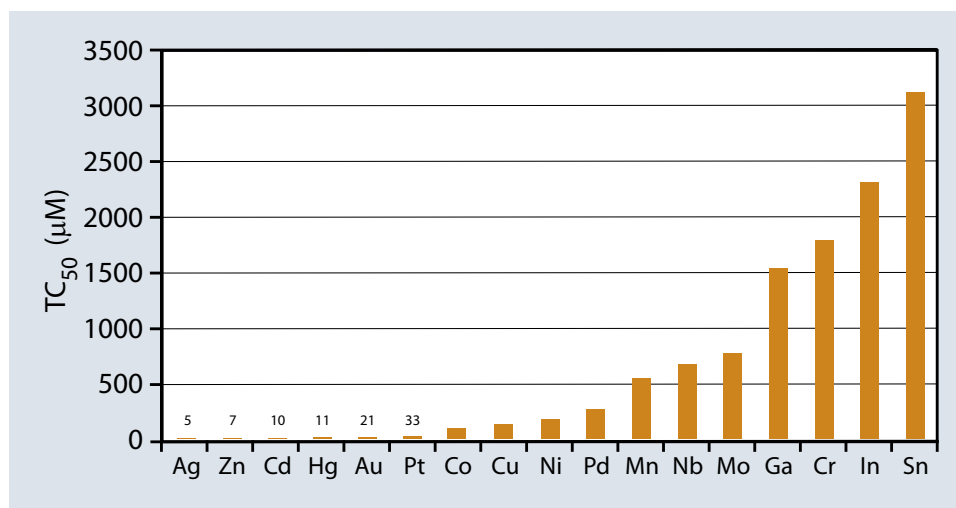
Inhaling metallic dusts from grinding or polishing beryllium-containing alloys, or fumes such as those encountered in casting beryllium-containing alloys, can cause berylliosis in individuals with a hypersensitivity to beryllium. The occupational data indicate that beryllium may increase the risk of lung cancer and other tumors in humans, especially for those working at beryllium-processing facilities. Thus dental lab technicians would presumably be at the highest risk of adverse effects from exposure to beryllium dust and vapors. The use of personal protection equipment (PPE) is necessary when metallic dusts in the dental laboratory arise during handling.

CRITICAL QUESTIONS

Which risks are associated with the handling of base-metal alloys? Which dental personnel are most likely to exhibit adverse effects to base-metal alloys?

Local Reactions

Figure 17-19 shows the concentrations of a series of metal ions that, in a cell-culture test, elicited 50% cell death (TC₅₀). The graph shows that various metal ions differ markedly in their



• **Figure 17-19** Cytotoxicity of different metal cations, expressed as the concentration that will kill 50% of the cells in culture (TC₅₀). Various metal cations elicit a large array of different cytotoxic reactions.

intrinsic (substance-specific) toxicity. In the *in vivo* situation, the amount of released metal ions together with their intrinsic toxicity will determine the biological effect. Copper or zinc has been added to the metal in metal-ceramic as an oxide former (Chapter 10, *Requirements of Metal Component*), which migrates to the surface and oxidizes during preparation of the metal prior to ceramic firing. These oxides on the surface release comparatively large amounts of copper and zinc if they are not covered with ceramic. The consequence would be gingivitis in patients observed next to crowns, such as that seen in Figure 17-11. Therefore the oxide layer on the alloys that is not covered by the ceramic must be removed.

The toxic potential of a high-gold alloy, two low-gold alloys, a high-palladium alloy, two Pd-Ag alloys, one Ni-Cr alloy, two Co-Cr alloys, and a 22k-gold alloy was tested by subcutaneous implantation in rats. The strongest responses were from the Ni-Cr alloy, and the weakest response was from the 22k-gold alloy. The high-gold alloy and the high-palladium alloy showed reactions similar to that of the 22k-gold alloy. However, the low-gold alloy and the Pd-Ag alloys ranked between the base-metal alloy and the high-gold alloys. This study and many other studies showed that the metallic ions released are responsible for much of the interaction behavior of dental alloys. However, no general prediction concerning the corrosion behavior and the biocompatibility based on the composition of the alloy alone is possible. However, severely cytotoxic alloys generally contain more nickel than those of biocompatible products.

Allergic Reactions

In a 2009 study, 206 patients underwent patch tests with the European baseline series because of a suspected contact allergy to dental alloys. Twenty-eight patients had positive reactions. The majority of positive reactions occurred for gold sodium thiosulfate, palladium chloride, and nickel sulfate, followed by amalgam, ammoniated mercury, and cobalt chloride, and then amalgam alloys and ammonium tetrachloroplatinate. Only 14 patients had a clinically relevant contact allergy on the oral mucosa (7 with oral lichen planus and 7 with stomatitis). The conclusions of the study were that contact allergies to dental alloys are infrequent.

Another study revealed that allergies to alloys in some patients were manifested not only by lichenoid contact lesions and contact

dermatitis responses but also pustulosis palmaris et plantaris, which may occur on the hands, the feet, or the entire body. Patch testing of 167 females and 45 males indicated that 148 (69.8%) patients had one or more positive reactions toward alloy components. The most common allergens were nickel, palladium, chromium, cobalt, and tin. A study of 60 persons documented that nickel has the highest allergenic frequency, followed by chromium, cobalt, silver, copper, palladium, platinum, and gold. A study suggested that dental patients could even be regarded as a risk group for metal allergies.

CRITICAL QUESTION

What should the clinician be aware of when using nickel-containing alloys?

Nickel Allergy

Nickel is a potent allergenic metal, with an incidence of allergic reactions between 10% and 20%. Reactions to nickel are more common among women, presumably because of the chronic exposure to nickel through jewelry, although the incidence among men is increasing. These reactions are probably underreported because they are often subtle and can resemble periodontal inflammation (Figure 17-8, B) or the erythema that results from excessive pressure on the palatal mucosa by metal frameworks. Not all individuals with nickel allergy will react to intraoral nickel, and it is currently impossible to predict which individuals will react. Because the frequency of nickel allergy is high, it is possible that individuals will become sensitized to nickel after the placement of nickel-containing alloys in the mouth.

The mechanisms of the high allergy frequency to nickel are not known, but there is probably a genetic component. In addition, the tendency of nickel-containing alloys to release relatively large amounts of nickel ions probably contributes to their allergenicity. This release is particularly high in acidic conditions, especially for Ni-Cr alloys with less than 20 wt% of chromium.

On the other hand, one study investigated 700 Finnish adolescents, 417 girls and 283 boys from 14 to 18 years of age, of which 476 (68%) had a history of orthodontic treatment with metallic appliances. The majority (91%) of the girls had pierced ears. Orthodontic treatment was equally common (67% to 70%) in the boys and the girls. The study consisted of patch testing

with palladium chloride and nickel sulfate, and a patient history obtained by a questionnaire and from patient records. The girls had a much higher frequency of allergic patch test reactions to nickel sulfate. The results suggest that orthodontic treatment does not seem to increase the risk for nickel hypersensitivity. Rather, the data suggest that treatment with nickel-containing metallic orthodontic appliances before sensitization to nickel (ear piercing) may have reduced the frequency of nickel hypersensitivity. This has been confirmed by other studies. The results of palladium chloride patch test are discussed in Ni-Pd Cross-Reactivity section.

Palladium Allergy

Metals of the platinum group exhibit a considerable allergenic potency. Palladium-based alloys have been associated with stomatitis and oral localized lichenoid reactions, and palladium allergy seems to occur mainly in patients who have also been sensitized to nickel. However, Wataha and Hanks concluded in 1996 that palladium-containing alloys do not generally pose an increased risk to the health of patients because of the limited dissolution rate of palladium from certain palladium alloys. However, one should note that the palladium in cast metals may react differently in single-phase compared with multiphase dental alloys, which tend to be less corrosion resistant. The corrosion products of these multiphase alloys may affect the allergenicity and the cytotoxicity of palladium-based alloys differently compared with single-phase alloys.

Ni-Pd Cross-Reactivity

Of the 700 Finnish adolescents discussed earlier in the Nickel Allergy section, 44 girls were palladium-chloride-positive, whereas only 4 boys had a reaction to palladium chloride. Of the 48 adolescents who tested positive to palladium chloride, 45 also had an allergic patch-test reaction to nickel sulfate. The results support the concept of cross-reactivity between nickel sulfate and palladium chloride. The co-reactivity of nickel and cobalt has also been reported.

In a 2018 study by [Mittermüller et al.](#) involving 500 patients (406 females and 94 males) with complaints concerning dental materials, 70 patients (14%) showed a verified allergy with clinical symptoms and a positive patch test to an intraoral alloy component. Out of the 500 patients, 234 (47%) had positive patch-test reactions to at least one of the tested possible allergens, with nickel (19.2%) and palladium (12.6%) being the most frequent allergens among these patients. Cross-reactivity to Ni and Pd was found in 39 patients, whereas positive reactions to Ni alone was seen in 57 patients and to Pd alone in 24 patients.

Titanium and Titanium Alloys

Studies have revealed that a surface layer of titanium oxide (mostly TiO_2 with small content of Ti_2O_3 and TiO) has the ability to coexist with living tissues and organisms. Based on these studies, one can conclude that titanium is relatively nontoxic and noninjurious. Recently, allergic reactions were claimed to be one of the causes of peri-implantitis. Limited clinical evidence shows that this might be true for very few cases. However, no standard patch test for titanium has yet been established. Another study links titanium nanoparticles to nonallergic peri-implantitis, and indeed, a comparatively high amount of such particles has been found around titanium implants. Ti nanoparticles are hypothesized to be phagocytized by macrophages that are present in the peri-implant tissues as a result of existing biofilm-induced inflammation. Because

macrophages cannot metabolize Ti particles, they secrete inflammatory mediators to attract more macrophages, thus enhancing the inflammation. However, the scientific evidence for such a scenario is limited.

Other Metals

Cobalt is another metal that, as a component of dental alloys, has been found to elicit allergic reactions in sensitized patients. Also, allergies to gold-based dental restorations have been more commonly reported. In the presence of gold alloy restorations the prevalence of gold sensitivity was significantly increased. The patch tests for gold sensitivity of a group of asymptomatic patients showed that 24 of 71 (33.8%) patients with dental gold appliances had a positive reaction to gold versus 7 of 65 (10.8%) of the patients with nongold appliances.

Symptoms of Metal Allergic Reactions

A review of 139 published cases of allergic reactions to dental metallic restorations showed that 99 patients suffered from local irritations in the form of gingivitis and stomatitis. Only 33 of 139 patients revealed general or remote extraoral reactions. When the restorations were removed, 82.7% of the patients recovered from the allergic reactions. Analysis of these data demonstrates that local allergic reactions to metals may often be underdiagnosed as inflammatory reactions. Interestingly, after intraoral application of alloys, both perioral (nickel allergy) and extraoral (cobalt allergy) skin reactions have been observed. In other studies, localized lichenoid reactions, swelling, and pain in oral soft tissues and lips have been reported. In several patients, gold ions caused an allergic contact gingivostomatitis, which was similar in appearance to erosive lichen planus. Many of these patients had a history of reactions to gold jewelry.

Immunotoxicity of Metals

The induction of immune mediators by metallic materials has been investigated using lymphocyte cell lines. Expressions of the inflammatory mediator interleukin 2 (IL-2) and the immune effector IgG by T and B cells were found after incubation with three copper-based casting alloys. The production of these immune mediators was altered by released cations. LPS-stimulated osteoblast-like cells increased the formation of interleukin 1 alpha (IL-1 α) and TNF- α after the cells were incubated with cobalt, chromium, and titanium. This study showed that metal ions disrupted cytokine release, osteoblast function, and the synthesis of type I collagen.

Cytokines can be released from unstimulated and stimulated peripheral blood mononuclear cells after incubation with chromium ions. In addition, chromium cations can reduce cell viability, DNA synthesis, secretion of IL-6, and expression of soluble IL-2 receptor. These results suggest that chromium may suppress the immune system.

Several metal ions (Ag, Au, Cu, Hg, Ni, Pd, Pt, and Zn) have induced the secretion of proteins from macrophages. Subtoxic concentrations of a nickel solution also induced an increase of IL-1 α and TNF- α secretion from unstimulated and LPS-stimulated THP-1 monocytes/macrophages. There is evidence that metallic components derived from cast dental prostheses can modulate the expression of various immunological factors. An increased expression of cytokines after LPS stimulation by various cell types indicates that bacterial toxins and cations released by corrosion may collectively cause inflammatory effects related to oral mucositis, gingivitis, periodontitis, and alveolar bone resorption.

Dental Ceramics

The oxides and related compounds in dental ceramics exhibit low dissolution in normal oral fluids and beverages. However, highly acidic or basic environments can increase the release rates of certain metal and silicon ions. For example, acidulated phosphate fluoride (APF) is known to corrode the surfaces of veneering porcelains and glaze and stain ceramics. This suggests that APF should not be used in patients who have ceramic or metal-ceramic restorations.

Adverse Reactions

Several investigators have demonstrated that unlike other dental materials, most dental ceramics do not induce an adverse effect when they contact the oral mucous membrane. Others have shown that glazed ceramics, which have been used in implant trials, caused very mild inflammatory reactions. These glazed ceramics were less irritating than resin composite or gold. One can conclude that minor observed irritations may be attributed to mechanical irritation (e.g., from roughened surfaces). Dental ceramics have successfully been used in patients with lichenoid reaction to replace the originally contacting material. Generally, polished or glazed dental ceramics accumulate significantly less biofilms on their surfaces than most other restorative materials.

Radioactivity of Dental Ceramics

Naturally occurring radioactivity has been detected in certain dental ceramics. No adverse effects that are caused by exposure to radiation from dental ceramics have been documented in the literature. A study reported that the beta-dose rates from natural radionuclides in feldspathic porcelains and glass ceramics were about 10 times higher than that of the background, whereas resin composites, alumina-based ceramics, and natural teeth exhibited negligible beta-dose rates. Concentration activities determined from gamma-spectrometry ranged from 2.01 to 2.9 Bq/g (becquerel per gram) ^{40}K . However, these activities are below the threshold limit of 10 Bq/g for ^{40}K . The specific activities of uranium and thorium were significantly lower than the levels reported in earlier periods when the addition of uranium to dental porcelain materials was used to enhance fluorescence. These results confirmed that patients with veneering ceramics and certain glass ceramics are subjected to higher dose levels (although well within safety limits) compared with the general population.

Hydrofluoric Acid

Etching of the glass phase of dental ceramics with 5% to 9% buffered hydrofluoric acid (HF) promotes bonding of resin composites to etched ceramics. HF formulated for dental usage is significantly more hazardous than other acids used in dental labs and in the mouth. Technicians and dentists should be well informed of the risks and the methods for dealing with accidental HF exposures.

Several fluorine-containing chemicals used in dentistry—such as ammonium fluoride, ammonium bifluoride, and sodium fluoride—may react with acid or water to produce HF. One should review the SDSs of all fluoride compounds to learn the safety precautions that are recommended to reduce the risk of HF exposure.

Exposure of Skin, Mucosa, and Eyes

Concentrated HF ($\geq 50\%$) is extremely corrosive and destroys skin or soft tissues upon contact and causes systemic fluoride poisoning. Exposure of the eyes to HF may result in blindness or permanent

eye damage. A significant concern regarding the use and possible exposure of tissue to low concentrations of HF for dental applications is that the pain or burning sensations may not be experienced until several hours after exposure. Because of this delayed effect of HF to produce severe tissue damage, possibly without pain, all tissues that have been exposed to HF should receive immediate first-aid care, medical evaluation, and follow-up evaluations even if the injury appears insignificant and no pain is experienced.

Inhalation of HF Fume and Ventilation

Inhaling HF fume can damage the lungs. Delayed effects may not be apparent for hours after the initial exposure. The U.S. Occupational Safety and Health Administration (OSHA) has set a limit for exposure to individuals for airborne concentrations to an average of 3 ppm HF over an 8-hour workday. To minimize inhalation of HF fume, gels and liquids should be used with adequate ventilation (e.g., fume hood).

Emergency Treatment

When eyes have been exposed to HF, they should immediately be irrigated at an eyewash station for at least 15 minutes with large volumes of water while the eyelids are held apart and away from the eyeballs. In all cases when the eyes have been exposed to acids, immediate medical attention should be sought.

If small areas of the hand or forearm have been contaminated, these areas must be immediately and thoroughly washed. If calcium gluconate gel is readily available, rinsing should be limited to 5 minutes so that application of the gel can be quickly initiated in order to limit the migration of fluoride ions. The calcium gluconate gel should be reapplied to the affected areas every 15 minutes. If calcium gluconate gel is not available, the affected areas should be rinsed for at least 15 minutes. Contaminated clothing must be removed and placed in a hood or plastic bag. Prompt medical attention should be sought in all instances of skin exposure to HF.

Calcium gluconate gel is available as a commercial product and is a topical antidote for HF residue on exposed skin. The gel combines with HF to form insoluble calcium fluoride, thereby preventing the extraction of calcium from tissues and bones. Calcium gluconate has a limited shelf life and should be refrigerated and replaced with a fresh supply after expiration. Disposable gloves should be used for applying calcium gluconate gel to the skin.

Glass-Ionomer Cements

Composition and Release of Substances

GICs (polyalkenoate cements) are acid-based cements that are mixed from a powder of finely ground glass (containing, e.g., calcium and sodium fluorophosphoaluminosilicate) and a liquid of polyacrylic acid ([Chapter 7, Glass Ionomer Cement](#)). Resin-modified glass-ionomer cements (RMGIs) are a heterogeneous group of materials that also contain water-soluble polymerizable monomers, such as HEMA and polyacrylic acid-modified methacrylate, and special catalysts. RMGIs polymerize by light activation. Glass ionomers release fluoride mainly after setting as an early burst, then decreasing asymptotically over time. Also, aluminum is liberated, and silver is liberated from silver-containing products. RMGIs release substantial amounts of monomers and catalysts.

Adverse Reactions of Conventional Glass-Ionomer Cements

No data have been published indicating any systemic toxic reaction after using conventional GICs in dental practice. These materials are nongenotoxic and nonmutagenic.

The Council on Dental Materials, Instruments and Equipment of the ADA reported in 1984 on severe pain after using GICs as luting agents, which made the removal of GIC-cemented restorations necessary. Possible causes include incorrect handling, such as pronounced drying of the prepared tooth prior to cementation; excessive pressure during cementation; or an insufficient thickness of remaining dentin. Since the implementation of the revised protocol, there have been no such reports published.

Nonset conventional GICs are cytotoxic, whereas set specimens are not or are only slightly cytotoxic. This parallels observations that these materials did not cause any pulp damage in medium or even in deep cavities in human teeth and those from experimental animals when used as restorative materials. Pulp reactions were only present when bacteria entered the cavity floor under the restoration. However, if placed directly on the exposed pulp, conventional GICs elicited severe pulp inflammation. This was probably attributable to the fact that conventional GICs do not completely set in contact with a wet surface. Therefore these materials should not be used for direct pulp capping. Conventional GICs do not cause any gingival or mucosal reaction, and they do not elicit allergies.

Adverse Reactions to RMGIs

As a result of the resin components (hydrophilic monomers), some RMGIs were reported to be genotoxic in vitro, although there are no reports on tumor formation caused by RMGIs. Some products are severely cytotoxic, even after the setting. In medium cavities of human teeth and in experimental animals, no pulp reaction was observed. In deep cavities, the data are inconsistent and depend on the individual product. In a study in human teeth, one RMGI showed pulp damage after the application of an RMGI. Therefore in deep cavities, a protective liner (e.g., calcium silicate cement) should be applied, and RMGIs should not be used for direct pulp capping. Recently, another RMGI product was tested in human teeth, which did not cause postoperative sensitivity or persistent pulp damage when applied as a liner in very deep cavities. This heterogeneity in the biocompatibility of different RMGI products emphasizes the need for the clinician to be familiar with the current scientific literature. Finally, because of the release of hydrophilic monomers like HEMA or TEGDMA, RMGIs may elicit allergic reactions in sensitized persons.

Natural Rubber Latex

Of particular interest in dentistry is the use of latex gloves and latex rubber dams, which expose both patients and dental personnel to this potential allergen.

Composition and Release of Substances

Natural latex products are made from a milky-white sap harvested from a rubber tree grown in tropical regions. Ammonia, which is added to the sap as a preservative, hydrolyzes and degrades the sap proteins to produce allergens. Adding sulfur in liquid latex and then heating transforms latex into an elastic compound by a process called *vulcanization*. The manufacturing process leaches the allergens by soaking the rubber products in hot water. The leaching water is changed repeatedly to decrease the concentration of the allergens, but leaching brings other allergens to the surface and, unfortunately, places the highest concentrations near the skin of the wearer. The cornstarch used in powdered latex gloves may also be the cause of glove allergy, although the allergen in the glove powder is usually latex released from the glove into the powder.

Thus the allergenicity of a given batch of latex will be dependent on how the latex was collected, preserved, and processed.

Allergic Reactions

The clinical symptoms associated with latex are contact dermatitis and local urticaria but also general urticaria, rhinoconjunctivitis, asthma, Quincke's edema, and in severe cases, anaphylaxis. Both type I and type IV reactions have been reported from contact with latex. After a 2016 review including data from the literature, the FDA suggested that the average prevalence of latex allergy worldwide remains at 9.7% among health care workers, 7.2% for susceptible patients, and 4.3% for the general population. Natural rubber latex (NRL) is the most noted cause of contact urticaria for dental personnel. Dental patients are also a special risk group because mucosal contact in sensitized individuals usually produces a stronger reaction than skin contact. Dental students showed an increasing incidence of type I allergies to latex gloves during the course of study.

Precautionary Measures

A thorough medical history specifically asking for a possible latex allergy is mandatory for any new patient in the office and should be documented throughout the course of treatment and follow-up. In cases of latex allergy, latex-free rubber-dam products and nitrile gloves must be used. Dental personnel should try to prevent a sensitization against latex by using nonpowdered, low-allergenic latex products or using latex-free products such as nitrile gloves. If an individual is sensitized, any contact with latex products has to be avoided. Again, nitrile gloves may be an alternative to latex gloves.

Patient Reports and Complaints of Adverse Effects

As mentioned in the discussion of postmarket surveillance, physicians, dentists, pharmacists, nurses, other health care professionals, and any other member of the public can report suspected adverse effects of medication or devices on the FDA MedWatch website. The devices also include restorations and implants. The number of cases related to dentistry is rather low; it is often a challenge to find the cause for the complaints and isolate the dental material that is responsible.

A national reporting system, the Dental Biomaterials Adverse Reaction Unit (DBARU), was established at the University of Bergen in Norway to monitor adverse reactions to dental materials in 1993. Similar systems were also established in Sweden in 1996, which were phased out in 2002, and in the United Kingdom in 1999. Some findings from the current literature are presented next.

A study comprising 500 patients claiming their complaints were caused by dental materials has been published. Subjective complaints reported by 490 patients mainly included burning mouth (44%), tooth-/jaw-ache (22%), and dry mouth (20%). The main objective intraoral symptoms were tongue anomalies (14%), gingivitis adjacent to restorations (12%), redness of the palate or the edentulous ridge (7%), oral lichen planus (6%), grayish discolorations (5%), lichenoid contact lesions (3%), and leukoplakia (2%). Only 46% of the patients showed objective symptoms. Patch tests confirmed the complaints or symptoms in 14% patients, with metals being the most frequent allergens.

Patients with non-oral-related complaints, such as weakness, headache, or intestinal problems, which have also been reported

in other studies, are a challenge for the clinician because these symptoms are unspecific, and there are many potential causes for these symptoms. For the symptoms of burning mouth or taste irritation, it should be considered that these are among the most common side effects of medical drugs. Dry mouth may also be a symptom for a patient's Sjögren syndrome. Therefore an interdisciplinary approach to the diagnosis and treatment of these patients is necessary.

The age and sex distributions of the studies discussed all show that elderly patients and females predominated. A reason for this specific age distribution may be the fact that patients in this age group are exposed to a large number of dental materials. One may assume that the high portion of females in the middle-aged and elderly age groups might be caused by endocrine changes. However, literature reviews show that the role of hormones in affecting oral health (e.g., burning mouth) and hormone replacement therapy is not yet confirmed. It has also been speculated that females are more likely to report adverse reactions than males.

CRITICAL QUESTION

What information is required to judge the safety of metallic, resin composite, and ceramic products?

Clinical Guidelines for Selecting Biocompatible Materials

Clinicians need to evaluate claims of the biological safety of new materials made by the manufacturers. With knowledge of biocompatibility issues, clinicians can make rational judgments about biological safety. Several critical steps described here will ensure an informed decision.

Define the Intended Use and Indications for Restorative Materials

As discussed previously, the intended use of a material plays a crucial role in the material's biocompatibility. Clinicians should inquire when the material is proposed for a new indication and if the material has been tested in the proposed use. If the material is used in a new way or new environment, more caution is advised. To minimize the risk of litigation resulting from unexpected adverse events, the lab technician and dentist must adhere to the instructions for use and use the material as indicated by the manufacturers. For other applications, such as off-label use, the practitioner is fully liable for any adverse effects that may occur. Furthermore, many dental materials are supplied by the manufacturer as a semifinal product, and the dentist finalizes the product through other processes, such as light curing a resin composite. Correct handling according to the instructions for use is essential for acceptable biocompatibility.

Identify the Main Components of the Material

The principal components of materials are listed in the SDS, but this list is not always complete, and elemental concentrations are not included. This is especially relevant for potential allergens, where even small amounts in the material may cause adverse reactions. Studies have shown repeatedly that a small

change in the composition or processing of a material can cause a significant change in the material's biocompatibility. In case of doubt, clinicians should ask the manufacturer for specific information. They also should request written information from the lab technicians certifying that the materials used are the ones the clinician has prescribed and that all instructions for use of the manufacturer have been followed. Generally, caution is advised in applying previous biological data and processing principles to new situations.

CRITICAL QUESTION

A sales representative introduces a new restorative material in your office or at a trade show. What do you need to know from him or her about the material's biocompatibility tests?

Evaluate the Safety and Performance of Dental Materials

In vitro or animal tests are sometimes difficult to relate to clinical applications. However, there are instances when clinicians do not have sufficient data from clinical trials to make an informed decision, so they must rely on in vitro or animal tests. Clinicians should not simply accept nondescript statements, such as "The material has been subjected to biocompatibility tests, and no adverse effects were observed," but should ask for the type of tests used. If clinical trial results are available, inquiring if the conditions and duration of the test are relevant for the practice is important.

The quality and relevance of usage test data depend on the fidelity of reproducing the clinical use. If animal or in vitro test results are the only ones available, then clinicians should question the design of these tests and the methods employed, making sure that testing conditions were as relevant as possible, including multiple types of tests performed under different clinically relevant conditions. A well-controlled comparison with existing similar types of materials is always preferable to an isolated test on one material. The known potential or claimed adverse effects of dental materials, such as those summarized in [Table 17-1](#), should be investigated periodically to ensure that patients will be presented with accurate information related to the benefits and risks of proposed treatments.

CRITICAL QUESTION

Based on the effect of substances eluted from dental materials on the immune system, who is responsible for deciding which materials are biologically safe for use—the patient, the dentist, the manufacturer, or the FDA?

Risks Versus Benefits of Dental Materials

The risk of using Ni-Cr alloy for crowns and bridges is the potential of releasing cations as a result of corrosion, especially at low pH values. These ions may be distributed in the oral cavity and may enter the systemic circulatory system. The benefit of using an Ni-Cr alloy over a high-noble alloy is the low cost and higher elastic modulus of the Ni-Cr alloy. In the case of *bis*-GMA-based resin, one of the potential adverse effects is the release of BPA. However, the quantity of BPA released is extremely small, and the sealing of pits and fissures in enamel surfaces is a highly effective means for preventing caries lesions or lesion progression in these

TABLE 17-1 Potential and Claimed Adverse Effects and Drawbacks of Dental Restorative Materials

Restorative Material	Potential Adverse Effects
Dental amalgam	Contact dermatitis or sensitization/allergic reactions to metal elements Localized lichenoid lesions Postoperative sensitivity Thermal sensitivity of pulp Symptoms of mercury toxicity, especially neurotoxicity Environmental concerns
Dental adhesives/ resin composites	Contact dermatitis or sensitization/allergic reactions to methacrylates Localized lichenoid lesions Estrogenic effects of bisphenol A Postoperative sensitivity from polymerization stresses and marginal gaps Pulp damage in deep cavities/pulp exposure Cytotoxicity or genotoxic effects
Dental alloys	Contact dermatitis or sensitization/allergic reactions to metals, especially nickel, cobalt, and beryllium Localized lichenoid lesions Thermal sensitivity of pulp Systemic effects of leached metal ions
Conventional glass-ionomer cements	Postoperative pain (luting materials) Pulp damage when placed on exposed pulp
Resin-modified glass-ionomer cements	Contact dermatitis or sensitization/allergic reaction to methacrylates Localized lichenoid lesion Postoperative sensitivity from polymerization stresses and marginal gaps Pulp damage in deep cavities/pulp exposure Cytotoxicity or genotoxic effects Systemic effects of other free monomers or leached substances
Dental ceramic	Respiratory effects from silica dust, excessive wear of antagonist tooth structure Radioactivity Toxicity of hydrofluoric acid

sites. Both examples depict the process of comparing the risks and benefits of a material.

Anamnesis (Patient's Account of Medical History)

Dental practitioners cannot simply follow a “cookbook” approach to select restorative materials for their patients. Instead, they must use their best clinical judgment based on scientific evidence and personal experience with the material and, more importantly, statements from patients, their physicians, and their previous dentists to ensure that all possible risks are minimized. For example, local and systemic allergic reactions to many alloys have been observed, with nickel being the most frequent allergenic element. Questioning the patient, parent, or caregiver about existing allergies would quickly eliminate certain alloys from consideration. Also, severe renal disease with impaired renal clearing function is

a contraindication for amalgam use. Information provided by the patient should be documented and regularly updated.

Treatment Planning

There is considerable variability in the treatment-planning process. The benefits and risks stated to patients by their practitioners are also likely to vary significantly from practice to practice. Obviously, some of the decisions will be based on accepting greater risks for the predicted benefits, whereas others will be based on a very conservative philosophy, which suggests that the risks of adverse effects should be exceptionally low. In some of these cases, when considerable risks exist, no treatment may be the best choice. For example, if some patients claim that they are allergic to several types of potential allergens, including metals, cosmetics, and foodstuffs, extreme caution is indicated to minimize related items. However, if the restorative treatment is essential to restore occlusion and function, these risks may be accepted, although informed consent procedures must still be satisfied before treatment begins. Once the practitioner makes a treatment decision, the patient should be informed of the benefits and risks of the proposed treatment and of any alternative treatments. Then, for medical and legal requirements to be satisfied, the patient must give his or her consent for the proposed treatment.

Risk Communication

Patients may ask the dentist before the treatment if the materials selected are safe. From a patient's viewpoint, safety often means that nothing bad will ever happen. However, this is not always possible. One may ask the patients about their hobbies or favorite sports and then inquire about the potential risks these activities may carry. The patients may soon realize that there is always a chance for adverse events to happen.

The clinician can refer to the fact that the probability of adverse effects from dental materials is generally low (0.3%). In contrast, the rate of adverse reactions toward cosmetic products has been reported as 12%. This means that the probability for an adverse reaction from contact with dental materials is about 40 times less than that with cosmetics if generally accepted good practice for patient treatment is followed. Finally, the risk should be “individualized,” meaning the clinician should explain to the patient the specific situation in the patient's case, such as allergies, cavity sizes, or the situation of the dentition in general. This specific and unique expertise enables the clinician to put Internet-derived information into clinical perspective for individual patients.

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Full Selected Readings for this chapter can be found on www.expertconsult.com.

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18

In Vitro Research on Dental Materials

OUTLINE

The Role of In Vitro Research

Clinical Relevance of In Vitro Tests

Standardization of In Vitro Test Methods

Limitations of Standards for In Vitro Research

Acknowledgment

KEY TERMS

Accelerated lifetime testing A research strategy that allows prediction of the performance of products over a long term based on tests conducted rapidly in the laboratory.

Accuracy The tendency of a test method to provide a result that is close to the correct result or the tendency of a statistical model to make a prediction that is close to a later observation.

Clinical relevance Conducting research in a way that closely mimics the conditions present in the clinic and in the patient.

Clinical significance A difference or change in product performance that actually affects the patient's quality of life.

Design of experiments A research strategy that allows efficient screening and optimization of design factors.

Effective volume The volume of a hypothetical test specimen with uniform stress distribution, such as in pure tension, that would have the same probability of fracture as an actual specimen of interest with nonuniform stress, such as a specimen tested in flexure mode.

Finite-element analysis An engineering analysis method for predicting the development of stress and strain in structures or the flow of energy or fluids through those structures.

In vitro research The testing of materials, drugs, and devices that is conducted in a basic science laboratory instead of being conducted in living test subjects.

Precision The tendency of a test method to consistently provide the same result.

Specification A document that describes one or more mandatory test methods and, in some cases, minimum acceptable levels of performance for a product.

Statistical significance A difference or change in product performance that is unlikely to be caused by random sampling error.

Technique sensitivity The tendency of some products to perform differently when manipulated by different operators.

In vitro research is the testing of materials, drugs, and devices that is conducted in a basic science laboratory instead of being conducted in living test subjects. This could mean measuring the degradation of materials when they are exposed in a test chamber that simulates the chemical composition and temperature of the oral environment, or testing could include measuring the mechanical response in a load frame or passing ultrasonic pulses through test specimens. In other cases, visible light may be measured as light is reflected and transmitted by a specimen to determine the color shade and translucency of the material. Reflection of infrared radiation and x-rays may also be measured to determine the molecular structure and the crystal structure of materials, respectively. In vitro tests may be conducted using synthetic materials to hold the specimen in place, or the specimen may be held by cadaver tissues. Virtual testing may be performed using three-dimensional (3-D) computer models to predict the performance of dental prostheses made from different materials. These are only a few examples of the many in vitro test methods used in the research of dental materials and devices. Some tests involve placing materials in a culture of living human or bacterial cells and

observing the cellular response. The interpretation of a living indicator provides a greater variety of factors to consider, so cell culture tests are discussed separately in [Chapter 17, Biocompatibility](#).

The Role of In Vitro Research

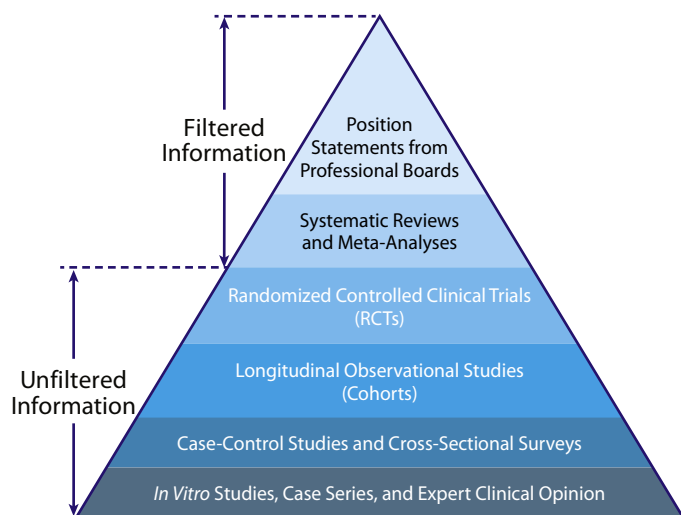
Students and professionals who are familiar with the topic of evidence-based medicine may recall that in vitro research is often placed low in the hierarchy of evidence. The vertical location of each layer in the evidence pyramid ([Figure 18-1](#)) indicates the relative weight that should be applied to that type of research in deciding whether a novel dental material or device performs well clinically. The width of each layer in the pyramid indicates the relative amount of that type of evidence that is available in the scientific literature. One important aspect of in vitro research is that there is a large volume of evidence available. However, each bit of in vitro evidence should be weighted lightly while making decisions about new dental products because those data—although intended to predict clinical performance—are not actually gathered in a clinical situation and may have little predictive power

individually. Despite these drawbacks, in vitro research still has an important impact early in the process of developing a dental product. In vitro results can bolster confidence in the safety of a product (as measured in terms of chemical durability, mechanical durability, and lack of toxicity) and in the efficacy of a product (as measured in terms of esthetics, dimensional accuracy, or antimicrobial activity, for example). This confidence is necessary before conducting clinical studies to avoid endangering human

test subjects and is necessary before conducting animal studies to avoid being wasteful in the allocation of those expensive and time-consuming studies.

CRITICAL QUESTION

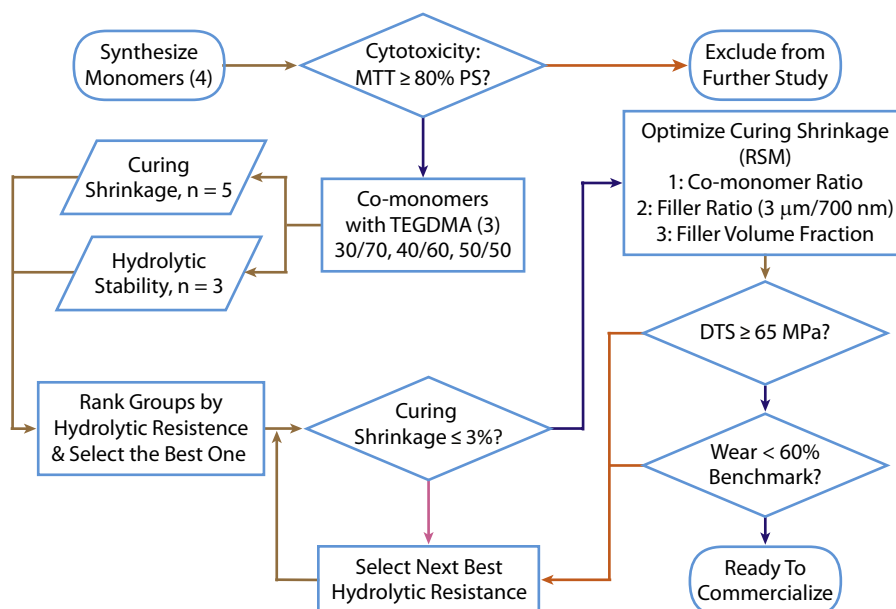
How can we gain confidence in the safety of a product prior to conducting clinical trials?



• **Figure 18-1** The hierarchy of evidence. In vitro studies are located in the bottom tier, indicating that there is a greater total amount of in vitro data than other types of data but also indicating that each in vitro study should be weighted lightly in clinical decision making.

Design of Experiments

There are many combinations of manufacturing parameters to be tested in the development of a new dental product. Besides the safety considerations discussed previously, the work requires a great number of specimens to be fabricated and tested. This means that it is important for in vitro tests to be precise, rapid, and inexpensive relative to clinical testing. Figure 18-2 shows a flowchart illustrating how the workflow might be conducted when optimizing the formulation of a dental composite that includes a novel comonomer. Optimization of a new dental composite is a topic that has been the focus of much previous research, so for researchers developing the flowchart, guessing as to which few design parameters will be the most important to control and vary is fairly easy. Other types of projects contain a greater number of variables. For example, dental implants sometimes have 25 different design features, and it may not be obvious from the outset which design features have the greatest impact on the performance of the implant. Even if each design parameter was tested in only two conditions, then a full factorial study would require fabricating and testing $2^{25} = 33,554,432$ groups of implants! In such cases, researchers employ powerful statistical methods with the assistance



• **Figure 18-2** Example flowchart for optimizing formulation of a dental composite made using novel comonomers. Orange arrows indicate the next block after rejection, and blue arrows indicate the next block after acceptance. Brown arrows indicate the next block after completion. Only the neat polymers that demonstrate a lack of toxicity according to the MTT assay (in comparison to tissue culture polystyrene) pass the initial screening. Each monomer that passes is developed into a series of copolymers with triethylene glycol dimethacrylate (TEGDMA). Only the copolymer formulation with the best hydrolytic resistance and with adequately low curing shrinkage passes the second screening and goes on to optimization of the filler particles. The final product must exhibit adequate diametral tensile strength and resistance to wear. (Courtesy Dr. Amol Janorkar.)

of research software (**design of experiments** [DOE] and **accelerated lifetime testing** [ALT]) or use engineering simulation software (**finite-element analysis** [FEA]) to conduct in vitro research as efficiently as possible.

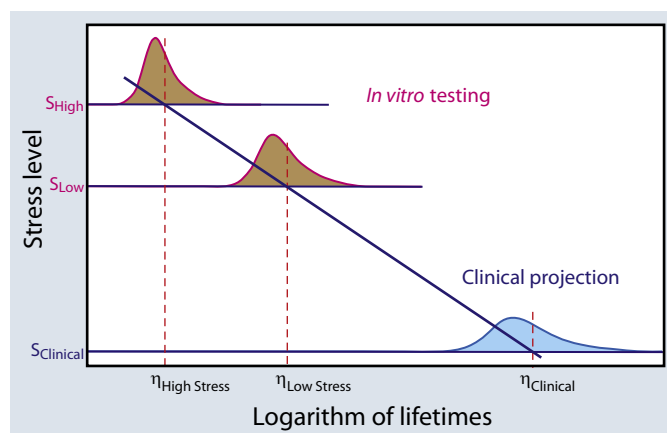
DOE is a research strategy that involves three steps: (1) screening design factors to determine which ones have the greater effect on performance, (2) identifying the combination of choices for the important factors that correspond to maximum possible performance (the optimal formulation; i.e., best balance of properties among those being investigated), and (3) identifying the combination of choices near the optimal formulation that results in the lowest variability in performance (the least technique-sensitive formulation). The first step in DOE is usually conducted using orthogonal arrays. Orthogonal arrays are lists of various combinations of choices for the design factors. Each combination corresponds to a different formulation or test group, and the list is constructed to be as short as possible by making the simplifying assumption that the importance of each design factor is independent of the choices for the other factors (no interactive effects). Orthogonal arrays can be quite efficient. For example, only eight test groups are needed to screen seven factors when the factors have two settings each. The second step in DOE involves using response-surface methods or sequential minimum-energy design to efficiently explore several possible choices or levels for each remaining factor. After the design space has been explored, the design corresponding to the maximum performance (strength, patient satisfaction, shelf life, etc.) or the minimum cost is identified. Compromise formulations can also be identified to satisfy multiple performance criteria simultaneously. The third step in DOE uses Taguchi robust design. This is similar to the second step, except minimum variability is treated as a performance objective, and a compromise formulation can be identified between minimizing variability and maximizing other performance measures. Minimizing variability is important for dental products because the dentists or dental lab technicians who will use the products have different levels of experience and have different personal habits of preparing teeth and manipulating materials. A technique-insensitive material system performs similarly regardless of the level of experience of the operator. In the case of a dental restorative material, for example, it is desirable for the product to have decreased **technique sensitivity** in addition to lending itself to forming restorations with a long average lifetime.

CRITICAL QUESTION

Why is it important for in vitro tests to be precise, rapid, and inexpensive compared with clinical testing?

Accelerated Lifetime Testing

ALT is used to predict the performance of dental materials over a long period in the patient's mouth based on tests conducted rapidly in the research laboratory. This is accomplished by testing material specimens at several stress levels (all of them being greater than the stress level of the clinical case). A statistical model is fit to the data to forecast the lifetime that would probably be observed at clinical stress levels (Figure 18-3). In ALT, the term *stress* is used in a general sense of the response of materials to an external stimulus and does not necessarily imply units of mechanical stress (such as MPa). Nonetheless, mechanical loading is the most common type of stressor used in ALT, but other challenges (i.e., temperature, humidity, etc.) may also be applied either singly or simultaneously.



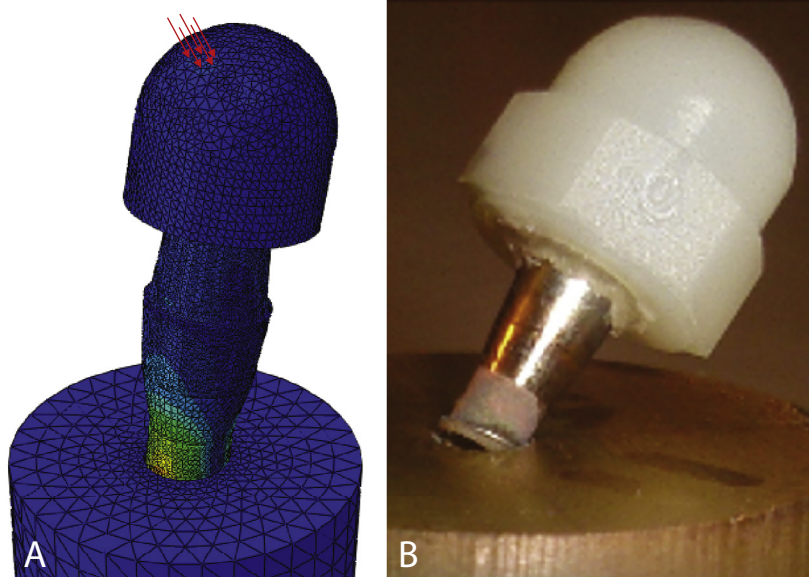
• **Figure 18-3** Regression model for accelerated lifetime testing (ALT). Specimens are tested in vitro at multiple stress levels, all of which are more severe than the stresses encountered in the clinical case. A Weibull distribution is fit to the lifetime data. For each in vitro stress level, the characteristic lifetime (η) by which 63.2% of the in vitro failures have occurred can be used in an extrapolation to predict the characteristic lifetime that the dental product would have if used in clinical cases.

ALT can be conducted as constant-stress accelerated lifetime testing (CSALT) or as step-stress accelerated lifetime testing (SSALT). In CSALT, each specimen encounters only one level of stress from the beginning of the test up to the moment when failure is recorded, such as one amplitude of stress in the case of a chewing simulation. In SSALT, a test specimen starts at a specified low stress. If the test unit does not fail at a specified time, stress on the unit is raised and held for a specified time, again. Stress is repeatedly increased until the test unit fails or the censoring time is reached. This leads to more rapid testing. However, researchers may have less confidence in clinical lifetimes forecasted from SSALT data than those forecasted from CSALT data.

It is important to remember that both types of predictions are extrapolations, and they include a great amount of uncertainty compared with clinical data. There is also a possibility that the levels of stressors, such as temperature or rate of mastication, may be elevated so greatly during ALT that degradation processes that would never occur in the oral cavity may be activated in addition to the processes that are being accelerated. In this case, inaccurate lifetime predictions are made. ALT can be used in conjunction with DOE by selecting clinical lifetime predictions as a performance measure to be maximized. In addition to predicting useful material lifetime in the oral cavity, ALT can also be used to predict the shelf-life of auxiliary dental materials such as alginate impression materials.

Virtual Modeling

FEA is an engineering analysis method for predicting the development of mechanical stress and strain or predicting the flow of energy (heat, electricity, magnetic fields, etc.) or the flow of fluids through structures. Current applications of FEA are aided by 3-D models and specialized computer software. A solid model may be fabricated using computer-aided drafting (CAD) software, or the model may be imported from a clinical scanner (micro-computed tomography [micro-CT]; Figure 18-4, A). This allows the modeling of precisely machined parts, such as dental implant components, and the modeling of parts with custom geometry, such as fixed dental prostheses and bones and other tissues (see Chapter 15, **Digital Technology in Dentistry**).



• **Figure 18-4** Fatigue test of dental implant system. **A**, Finite-element model to predict the stress distribution in a dental implant. The heat map (known to researchers as *stress contour plot*) shows the magnitude of stress on each location of the implant, where hotter colors correspond to high levels of tension and cooler colors correspond to compression or low levels of tension. **B**, The physical implant specimen fractured in vitro during accelerated lifetime testing. Fracture originated at the location that was predicted by the finite-element model to have the highest stress. (Courtesy Dr. Yuanyuan Duan.)

The solid model is divided into thousands or millions of minuscule volume elements (Figure 18-4, *A*), and each element is assigned properties according to the material that constitutes that portion of the model. Using a greater number and smaller size of elements results in more accurate predictions but also requires more computing time and/or power. An important test of accuracy that is often neglected involves solving an FEA problem multiple times, with an increasing number of elements in each iteration. The results should converge on a limiting value. If such a convergence test is not present with the reported results, then the FEA predictions may not be accurate. The absolute level of stress predicted cannot be trusted in this case, but the pattern of the stress distribution still provides useful information regarding the locations of higher and lower stress concentration in a dental prosthesis (Figure 18-4, *B*).

The most common results to be predicted using FEA are the stress and strain resulting from mechanical loading. That type of analysis requires inputting material properties of Young's modulus and Poisson's ratio (Chapter 4, *Stress-Strain Properties*). The accuracy of material properties depends on the method used to measure them, and if inaccurate material properties are input to the model or if invalid assumptions are made regarding the anisotropy (direction dependence) of these properties, then the FEA results will be invalid. Stress and strain results can be exported to additional postprocessing software that combines these results with material fatigue testing data to predict the probability of failure by a specified elapsed time for each element in the finite-element model and to predict the probability of failure for a dental prosthesis or implant as a whole. FEA can be used in conjunction with DOE by selecting the probability of failure as a performance measure to be minimized.

CRITICAL QUESTION

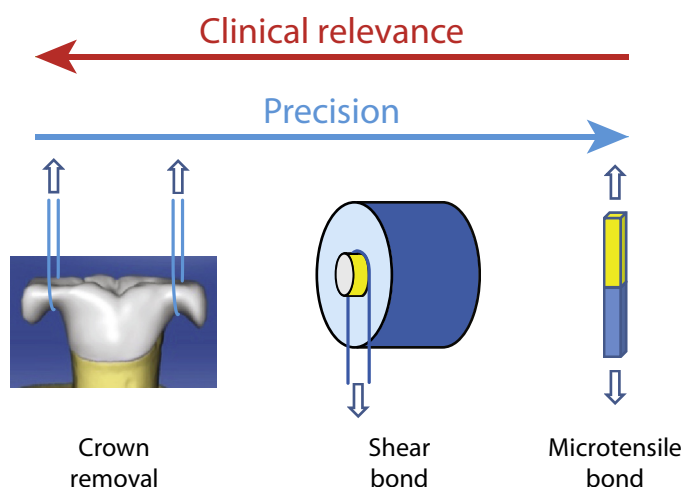
What factors lead to a lack of accurate forecasting in ALT?

Clinical Relevance of In Vitro Tests

For some classes of dental materials, there are in vitro tests that can predict the performance of a given formulation or the comparative ranking for different formulations, but performance can be difficult to predict for other applications or classes of materials. For example, David Mahler showed that marginal fracture or “ditching” in dental amalgam fillings can be predicted by tests of creep resistance. His finding was that the more ditching-resistant amalgams lacked a γ_2 phase in the microstructure, and that the formation of the γ_2 phase could be avoided by increasing the copper content of the amalgam alloy. The resulting high-copper amalgams produced dental fillings with greatly improved longevity. On the other hand, Jack Ferracane compiled material property data from a variety of in vitro tests, and he concluded that the clinical failure of composite restorations is a complex, multifactorial process that cannot be predicted from an in vitro test or a combination of tests. However, in the early development and screening stages of new dental materials, in vitro tests remain the only tools we have and thus the best tools that we can use to make an educated guess regarding which material formulations will exhibit superior performance.

Precision Versus Clinical Relevance

There are often several competing in vitro tests that can be used to measure a single material property. For example, dentin bond strength can be measured by a microtensile bond-strength test, a button shear test, or a crown-removal test (Figure 18-5). There are even several variations in the geometry of the test specimen or the method of load application to choose from when conducting each of these three test methods. In these cases, there is usually not a single test method that has superior performance in testing all kinds of hypotheses related to a particular material property. Rather, the various test methods are usually distributed across a



• **Figure 18-5** Spectrum of in vitro testing methods. The test configurations shown are different options for determining the strength of bonding of dental adhesives. The tests are sorted by their clinical relevance and the precision of strength values. The direction of the arrow show the increase of clinical relevance from right to left (red arrow) and the increase of precision of strength values from left to right (blue arrow). (Courtesy Dr. Susana Salazar Marocho.)

spectrum that has a high level of **clinical relevance** on one end and a high level of **precision** on the other end.

In the case of dentin bond-strength evaluation, the removal of an actual dental crown from a real tooth (that was previously extracted with permission of the patient) may have more clinical relevance than the other two test methods. Obviously, the bonded area and the configuration of the crown-removal test specimen are the same as in the clinical case, which means that the operator will have the opportunity during specimen preparation to create a similar number and size distribution of flaws that would be present in a clinical cementation. In addition, the line angles are similar to those in the clinical case, which means that there will be a similar profile of stress concentration. The prepared specimens should also have a similar thickness of the cement layer, marginal gap size, and opportunity for hydrolytic degradation when stored in a simulated environment. The C-factor (ratio of bonded to nonbonded surface area) is also similar to that of the clinical case, which provides the same opportunity for polymerization-induced stress to develop at the margin (Chapter 5, **Cure Shrinkage and Managing Shrinkage Stress**). However, testing an actual dental crown also leads to variability from one specimen to the next because teeth are unique in their overall shape, the dimensions of their dentinal tubules, and the degree of mineralization. Thus a lack of precision in the test results can be expected for the crown-removal test, and this may make detection of any improvements in bond strength resulting from novel bonding treatments impossible if those improvements are small.

The microtensile bond-strength test (μ TBS) is at the other end of the spectrum. μ TBS specimens are fabricated by exposing a flat cross-section of dentin, bonding a restorative material to that flat section, and then slicing the resultant layered specimen julienne-style by making a series of parallel cuts along both orthogonal directions. The final specimens are minuscule in size and are shaped like sticks with the bonded interface perpendicular to the long axis of each stick. There is a high degree of precision because the interface is flat and because several specimens are prepared from the same tooth. Different bonding protocols can even be compared on the same tooth by placing a barrier in the middle of the sectioned tooth during bonding. However, the

μ TBS specimens do not share the similarities with the clinical case listed previously for the crown-removal test. The button shear test is somewhere in between the crown-removal and μ TBS tests and is not as well suited for precision testing or for clinically relevant testing compared with either end of the spectrum. There are some difficulties with preparing buttons having consistently equal surface area. Recall from the discussion of shear stress in Chapter 4, **Shear Stress** that stress distribution upon mechanical loading is not a constant stress across the adhesive-tooth interface (nor even pure shear or pure tension at the interface). Whether the button is loaded using a wire loop (Figure 18-5), flat blade, or a rounded blade, the shear bond test does not provide much precision, and it also does not closely resemble the clinical case.

CRITICAL QUESTION

When is it more important to use a precise test instead of a clinically relevant test?

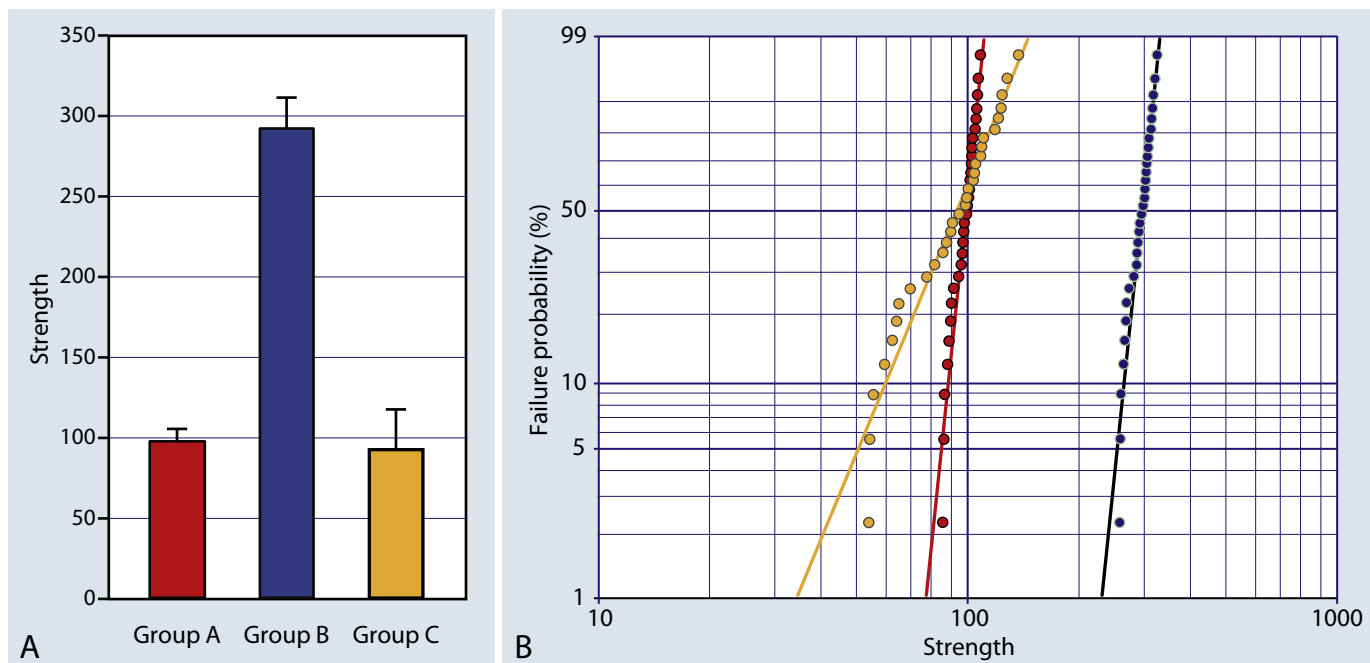
The Weibull Size Effect

Recall da Vinci's observation that the tensile strength values of iron wires decreased as the length of the wire increased (Chapter 4, **Fracture of Restorations**). The work of Griffith showed that the nominal strength of the material was dependent on the size of the flaws distributed within the material. Consider that each unit of volume in a test specimen contains a variety of microscopic flaws, with a somewhat random distribution of flaw sizes. Thus a larger specimen having more units of volume also has a higher probability of containing a large flaw than does a specimen with a smaller volume. All other factors being equal, the strength of a specimen is controlled only by the size of the specimen's largest flaw, so large specimens tend to have lower strengths on average. Griffith's work explained the physical basis of da Vinci's observation but did not provide a quantitative relationship between the physical size of the specimen and the strength value. That quantitative relationship was later provided by Waloddi Weibull's extreme value distribution (known today as the *Weibull distribution*).

In ranking the strengths of different prosthetic materials or in comparing bond strengths yielded by different dentin bonding protocols, it is important to compare data from similarly sized specimens to avoid the influence of the size effect on the strength values. From the bond-strength test examples presented earlier, one should note that different types of tests use different sizes of specimens, making the comparison between testing groups difficult. When the size of the test specimen is smaller than the actual size of the restoration in service, the comparable material strength values in the form of a restoration would be of interest to the manufacturers. The statistical approach of Weibull analysis discussed in Chapter 4, **Weibull Modulus**, provides a means of estimating the strength of the objects made of the same material but different in specimen volume from those tested.

If two groups of specimens made of the same material differ in size, then eq. 1 can be used to convert from the mean strength (σ_1) of a group of specimens having one volume (V_1), to the mean strength (σ_2) that would be expected from the specimens of the same material prepared in the same way but having a different specimen volume (V_2):

$$\frac{\sigma_1}{\sigma_2} = \left(\frac{V_2}{V_1} \right)^{1/m} \quad (1)$$



• **Figure 18-6** Statistical analyses of strength values of three hypothetical dental products. Each data set consists of 30 specimens, and the values are generated by a random generator. **A**, Bar chart showing the means and standard deviations of strength. **B**, Lognormal distribution probability plot (or Weibull graph) showing the strength distributions for the same three products. A product with a higher mean strength will have a line farther to right on the Weibull graph. A product with a smaller standard deviation will have a line with a steeper slope on the Weibull graph. If the probability axis is plotted in interval scale and strength axis is plotted in ordinary scale, each curve will be shaped like the bacterial growth curve shown in the Weibull analyses of Figure 4-16.

The exponent (m) in eq. 1 is known as the *Weibull modulus*, and the determination of this value has been discussed in detail in Chapter 4, *Weibull Modulus*. Essentially, the Weibull modulus is a measure of variability in specimen strengths—similar in purpose to the standard deviation except having larger values for specimen groups with less variability. Figure 18-6 shows a comparison of a typical bar chart showing means and standard deviations of strength data for three hypothetical materials and the corresponding Weibull plots comparing the same set of data. The Weibull plot with the lowest slope (gold) corresponds to the lowest Weibull modulus and belongs to the group that has the highest standard deviation. The Weibull plot that lies farthest to the right (blue) corresponds to the group with the highest average strength. Lifetime data of restorations can also be characterized using a Weibull distribution.

The use of the conversions described previously requires that the stress distribution be uniform across all portions of a specimen, as in the pure tensile test mode. If the stress distribution within the object of interest is not uniform, such as in the bending test mode, the *effective volume* of the specimen is calculated and used instead of the actual volume. The effective volume is the volume of a hypothetical tensile test specimen that exhibits uniform stress distribution when subjected to loading, and that has the same probability of fracture as the test specimen exhibiting nonuniform stress distribution when loaded. The effective volume is dependent on the loading method and can be determined by a calculus operation with respect to the volume of the specimen or the prosthesis. The results have already been published for the common types of test specimens and loading conditions; for example, the formulas for a cylindrical rod, a rectangular beam, and a square beam loaded in flexure were published in 2003.

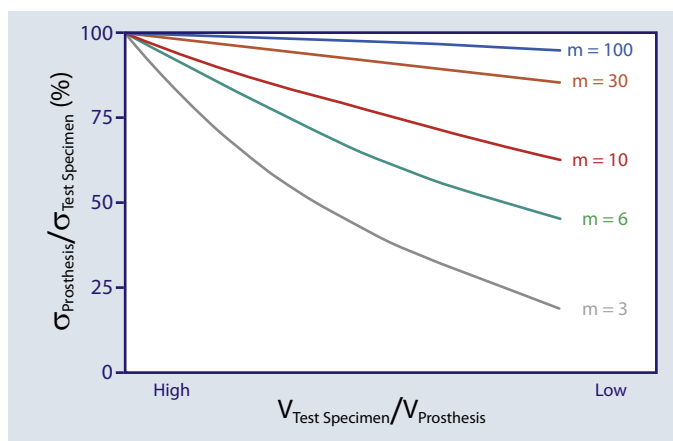
The graph in Figure 18-7 illustrates the conversion of specimen strengths according to eq. 1 for several different values of Weibull moduli. In addition to converting between the results of different test methods, eq. 1 or Figure 18-7 can be used to estimate the strength of clinically placed prostheses from strength data gathered in vitro.

CRITICAL QUESTION

When should a statistically significant difference between products be disregarded?

Clinical Significance Versus Statistical Significance

When interpreting the results of in vitro tests and using them as a basis for clinical decision making, it is important to keep in mind the difference between *clinical significance* and *statistical significance*. Statistical significance is achieved when the difference between two dental products is greater than the difference that is likely caused by random sampling error. For example, suppose 20 denture teeth of the same manufacturer and model are tested, and this group of specimens has a chipping resistance of 120.0 ± 0.1 N (mean \pm standard deviation). Twenty more denture teeth from a different manufacturer are determined using the same protocol to have a chipping resistance of 121.0 ± 0.2 N. A statistician would calculate that there is a highly significant difference between these two products ($p < 0.001$), which indicates that the 1.0-N difference between our sample means of 120.0 and 121.0 N has a greater than 99.9% chance of being caused by a



• **Figure 18-7** Graph illustration of eq. 1. The graph shows the effect of in vitro test specimen size on the ratio of in vitro product strength to the strength when used in a clinical application having a different volume of material. Specimens, prostheses, and implants having larger volumes of material are weaker (assuming uniform stress distribution). Products having a high Weibull modulus (m) are less sensitive to differences in the volume of material.

difference between the manufacturers and a less than 0.1% probability of being caused by random chance during specimen selection. In this example, the ability to detect such a small difference as being highly significant is made possible by the low standard errors of both groups. This happens during in vitro research when a very precise test method is used. The ability to detect statistical significance with a small difference between groups also happens during clinical research reports when a meta-analysis includes a large number of studies and therefore patients. The conclusion that the manufacturers have products of differing quality is scientifically sound. However, changing clinical decisions based on this small difference would not make sense. The ability of a removable denture to resist chipping from a bite force of 121.0 versus 120.0 N is clinically insignificant because this difference would not be expected to affect the benefit that the patients receive from one product versus the other product, especially considering that chipping resistance is only one of many performance criteria for removable dentures (esthetics, fit, chemical stability, etc.). A difference is clinically significant when this difference would make a noticeable impact on the average patient, and smaller differences should not influence clinical decisions even when they are shown to be statistically significant.

Standardization of In Vitro Test Methods

One of the major advances in the knowledge of dental materials and their manipulation began in 1919, when the U.S. Army requested the National Bureau of Standards (now known as the National Institute of Standards and Technology or NIST) to establish **specifications** for the evaluation and selection of dental amalgams for use in federal service. These test reports were received enthusiastically by the dental profession, and similar test reports were subsequently requested for other dental materials. All findings were published and became common property under this arrangement. In 1928, dental research at the National Bureau of Standards was taken over by the American Dental Association (ADA). In this section, we will describe the role of the ADA and international organizations in establishing standards.

ADA Specifications and Acceptance Program

The ADA, accredited by the American National Standards Institute (ANSI), is also the administrative sponsor of two standards-formulating committees operating under the direction of the ANSI: the ADA Standards Committee on Dental Products (SCDP) and the ADA Standards Committee on Dental Informatics (SCDI). The ADA SCDP develops specifications for all dental materials and instruments, with the exceptions of drugs and x-ray films. The ADA Council on Scientific Affairs (CSA) is also separately responsible for the evaluation of drugs, tooth-cleaning and tooth-whitening agents, therapeutic agents used in dentistry, dental equipment, and dental x-ray film.

Working groups of the ADA SCDP or ADA CSA develop the specifications. When a specification has been approved by the ADA SCDP and the ADA CSA, this specification is submitted to the ANSI. On acceptance by this body, the specification becomes a U.S. national standard. New specifications are continually being developed to apply to new products. Likewise, existing specifications are periodically revised to reflect changes in product formulations and new knowledge about the behavior of materials in the oral cavity.

In 1930, the ADA Council on Dental Therapeutics established the ADA's Seal of Acceptance program to promote the safety and effectiveness of dental products. When the ADA CSA assumed responsibility for developing specifications (standard test methods) in 1966, the CSA also initiated the certification of products that meet the requirements of these specifications. The Seal of Acceptance program incorporates these specifications in the evaluation of dental products. When a product is classified as *accepted*, the manufacturer is permitted to signify on the label of the product that notation "ADA Accepted."

In 2005, the ADA decided to phase out the professional products component of the Seal of Acceptance program. Instead, a decision was made to publish a product evaluation newsletter for ADA member dentists that focused on a specific category of professional products in each article. This newsletter, called the *Professional Product Review*, was initiated in July 2006, and the final phase-out of the ADA acceptance seal for professional products occurred on December 31, 2007. Keep in mind that the acceptance program for oral care products sold to the general public, including toothpaste, dental floss, toothbrushes, mouth rinse, and so forth, is still in place.

International Standards

Two organizations, the Fédération Dentaire Internationale (FDI) and the International Organization for Standardization (ISO), are working toward the establishment of specifications for dental materials on an international level. The ISO is an international, nongovernmental organization whose objective is the development of international standards. This body is composed of national standards organizations from more than 80 countries. ANSI is the U.S. member of the ISO. As of 2018, the ISO had 249 technical committees (TCs). Originally, the FDI initiated and actively supported a program for the development of international specifications for dental materials. A request by the FDI to the ISO that it should consider FDI specifications for dental materials as ISO standards led to the formation of the technical committee ISO TC 106—Dentistry. The responsibility of this committee is to standardize terminology and test methods and to develop international standards for dental materials, instruments, appliances,

and equipment. More than 180 dental standards have been published by TC 106, and 55 dental standards are currently under development. The following four subcommittees cover most of the dental restorative materials products included in the ISO standards program under the direction of TC 106:

TC106/SC1: Filling and Restorative Materials. The following 10 working groups (WGs) are included: WG1—Zinc Oxide/Eugenol Cements and Noneugenol Cements; WG2—Endodontic Materials; WG5—Pit and Fissure Sealants; WG7—Dental Amalgam; WG9—Polymer-Based Restorative Materials; WG10—Dental Luting Cements, Bases, and Liners; WG11—Adhesion Test Methods; WG13—Orthodontic Products; WG14—Orthodontic Elastics; and WG15—Adhesive Components.

TC106/SC2: Prosthodontic Materials. The following 18 working groups develop standards for prosthodontic materials: WG1—Dental Ceramics; WG2—Dental Base Alloys; WG6—Color Stability Test Methods; WG7—Impression Materials; WG8—Noble-Metal Casting Alloys; WG10—Resilient Lining Materials; WG11—Denture Base Polymers; WG12—Corrosion Test Methods; WG13—Investments; WG14—Dental Brazing Materials; WG16—Polymer Veneering and Die Materials; WG18—Dental Waxes and Baseplate Waxes; WG19—Wear Test Methods; WG20—Artificial Teeth; WG21—Metallic Materials; WG22—Magnetic Attachments; WG23—Chairside Denture Base Relining Materials; and WG24—Frictional Retention.

TC106/SC8: Dental Implants. The eight groups in SC8 are as follows: TG2—Dental Implant Terminology; WG1—Implantable Materials; WG2—Preclinical Biological Evaluation and Testing; WG3—Content of Technical Files; WG4—Mechanical Testing; WG5—Dentistry – Implant Terminology; WG6—Preclinical Performance Requirements; and WG7—Evaluation of Connective Interfaces of Dental Implant Systems.

TC106/SC9: Dental CAD/CAM Systems. The five working groups in SC9 are as follows: WG3—Digitizing Devices; WG4—Interoperability; WG5—Machined Devices; WG6—Machinable Blanks; and WG7—Test Methods for Additive Manufactured Dental Products.

When the term *dental materials* is used, dental restorative materials are often foremost in mind, but it should be clear from the list of working groups that there are many auxiliary materials and many preventative materials that also require testing. For some of those materials, in vitro tests are needed to gauge a wide variety of material properties, including mechanical, chemical, magnetic, and optical properties, among others. The working groups are continuing to change year to year as new categories of materials are being introduced, and some categories of materials are becoming obsolete.

CRITICAL QUESTION

Why would a specification require using a test that is not the most precise test method?

Limitations of Standards for In Vitro Research

It is also important to know the functions that standards and specifications are not meant to perform. The minimum performance limits specified in standards are not representative of the performance of the average product currently on the market. They are

instead minimum acceptable thresholds for safety and satisfactory performance. In addition, the test methods described in standards and specifications are not necessarily the best or the most precise methods. Standard tests are limited in that they generally use inexpensive equipment and supplies that are readily available in most laboratories, and they generally do not require complex statistical tests. In addition, a standard is not adopted unless this standard can be agreed upon by many experts having a wide variety of perspectives. This means that standards are only the greatest common factor between the different methods that are used successfully in multiple laboratories. In addition, there are some important material properties for which there is no standard test. This could be caused by a lack of agreement among experts, by a lack of timeliness in the approval process, or by the invention of a novel dental product that cannot be adequately tested using any currently known tests. For example, fracture toughness is an important metric for comparing ceramics to be used in fixed dental prostheses because fracture toughness is independent of surface finish, testing environment, and loading method. The ISO standard for dental ceramics (ISO 6872:2015) does not identify or require a single test for fracture-toughness testing. Instead, the standard contains an informational appendix that discusses the advantages and disadvantages of several fracture-toughness test methods. A fracture-toughness test typically begins with scoring or precracking the test specimen, and the tip of this precrack should be smaller than the crystalline grains that constitute the material microstructure. Otherwise, overestimation of the fracture toughness will result. However, the newest and most durable ceramic materials have submicron grain sizes, and some of the most popular test methods cannot create a precrack that is sharp enough to accurately assess the fracture toughness of those materials.

Standards perform an important function in communication between researchers and in government regulation of products, as described previously, but the scientific literature often contains results from different in vitro tests that are more precise or that more closely mimic clinical conditions. The editorial board of the journal *Dental Materials* has begun assigning teams of experts to coauthor guidance documents for testing material properties that have proven challenging in the past. These guidance documents describe the test methods that currently have the maximum possible accuracy or precision in lieu of standards that use easily obtainable equipment. In some cases where a standard allows a range of test parameters, the guidance document explains why one specific parameter setting is preferable over another. For example, the ISO standard for fatigue testing of dental implants (ISO 14801:2016) allows the holder, which simulates bone holding the implants, to have any mechanical properties so long as the Young's modulus (stiffness) of the specimen holder is higher than 3 GPa. This is conveniently close to the Young's modulus of many epoxy and acrylic products that are already present in most material sciences laboratories. Unfortunately, this value is much lower than the stiffness of a typical jawbone and does not mimic the difference in stiffness between the cortical and cancellous layers or the anisotropy within a given layer. Computer models show that this difference in stiffness of the holder material has a strong effect on the results of the mean lifetime prediction of implant systems, so holder materials that more closely mimic real bone would be preferable. In some cases, the most advanced test methods are not feasible for use in many laboratories, and simple standard tests must be used. For example, tests that employ cyclic fatigue loading more accurately mimic the clinical situation, and the use of sliding contact during the load cycle has been shown to give a different test result than loading methods that are less clinically relevant. Equipment that

is capable of precisely controlling the cyclic loading of specimens on both horizontal and vertical axes simultaneously can be expensive to acquire and maintain, so ISO 6872:2015 specifies the use of only monotonic (noncyclic) vertical loading, and this remains an important common factor for comparing results regarding the strength of ceramics used in fixed dental prostheses.

Selected Readings

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Full Selected Readings for this chapter can be found on www.expertconsult.com.

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19

Clinical Research on Restorations

OUTLINE

What Is Evidence-Based Dentistry?

Level of Evidence in Evidence-Based Dentistry

Clinical Analysis of Survival and Acceptability

KEY TERMS

Case-control studies Type of study that examines two groups at a point in time, usually groups with and without disease or intervention, and makes inferences from these.

Evidence-based dentistry An approach to oral health care that requires the judicious integration of systematic assessments of clinically relevant scientific evidence, relating to the patient's oral and medical condition and history, with the dentist's clinical expertise and the patient's treatment needs and preferences.

Fractography The study of fractured surfaces of materials.

Prospective analysis study Type of study that plans interventions, examines the results of these interventions over a period of time, and makes conclusions.

Randomized controlled clinical trial A prospective study that randomizes participants and employs a control group.

Retrospective study Type of study that examines past occurrences and interventions and deducts results and conclusions.

One of the most difficult areas in dental materials research is the ability to predict their clinical performance through in vitro testing methodologies. The oral environment is almost impossible to simulate in a laboratory setting because of the many variables that need to be introduced, such as occlusal forces, the pH of the surrounding environment, diet, the buffering capacity of saliva, and muscle and soft tissue cleansing action. As such, most in vitro testing methodologies evaluate how a material responds to a specific testing condition, and the experimental data are used to differentiate between materials. The true test for a restorative dental material is clinical performance, which includes longevity and predictability of use. In recent years, there has been a push from the medical community to implement evidence-based dentistry in dental education and practice.

What Is Evidence-Based Dentistry?

Evidence-based dentistry (EBD) is defined as an approach to oral health care that requires the judicious integration of systematic assessments of clinically relevant scientific evidence, relating to the patient's oral and medical condition and history, with the dentist's clinical expertise and the patient's treatment needs and preferences. The types of evidence were ranked, with laboratory or standardized testing as being the lowest tier of evidence, followed by in vivo observations in the form of clinical studies and case studies. The highest form of evidence is the controlled, randomized clinical trial, where clinical interventions are allocated by chance and evaluated based on performance. The randomization eliminates the effect of multiple patient variables, which can skew results.

CRITICAL QUESTION

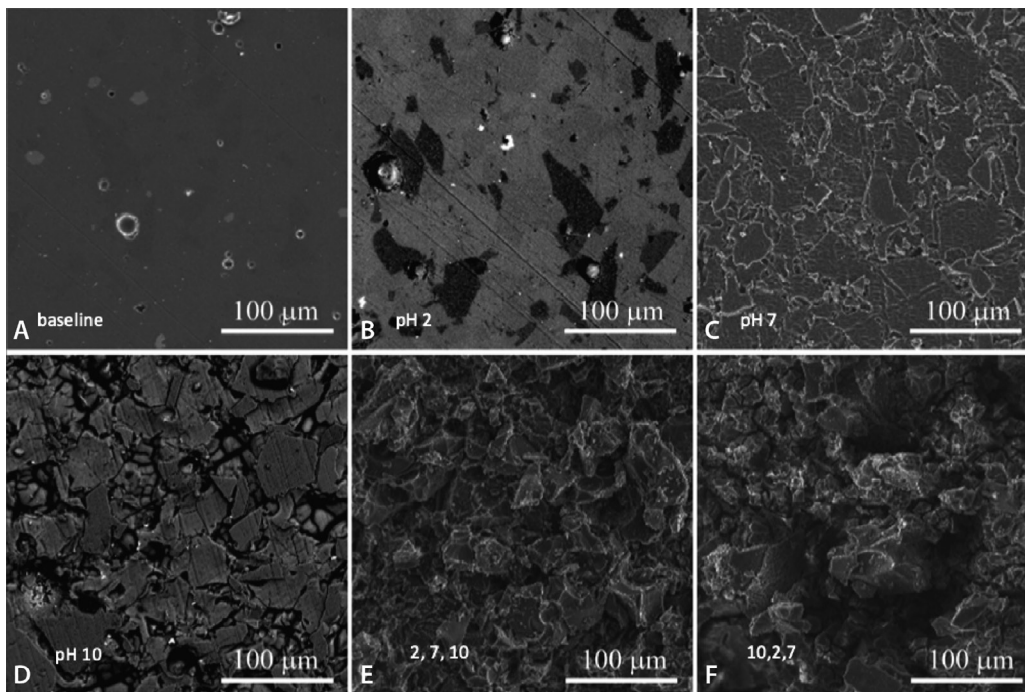
Why are clinical trials essential in testing the performance of dental biomaterials?

Level of Evidence in Evidence-Based Dentistry

Among the available hierarchy of evidence, position statements from professional boards, supported by systematic reviews and meta-analyses of **randomized controlled clinical trials** (RCTs), contribute to the highest level of evidence, followed by RCTs and cohort studies. These are followed by **case-control studies**, cross-over studies, cross-sectional studies, case studies, and case reports. Finally, there are animal research and in vitro laboratory testing. At each level of evidence, there is a body of knowledge, but not all levels are equally useful for making patient care decisions. As we progress up the pyramid (see **Figure 18-1**), the number of studies and, correspondingly, the amount of available literature decreases while at the same time, their relevance to answering clinical questions increases. From a dental material point of view, we will discuss the evidence in three categories: in vitro testing, observational studies, and randomized control clinical studies.

In Vitro Testing

In **Chapter 18**, the role and relevance of in vitro testing methodologies were discussed. Although necessary, these standardized tests often evaluate a limited number of variables in one test condition and are not representative of the true oral environment.



• **Figure 19-1** Scanning electron microscopy of ceramic surfaces before and after 27-day immersion in buffer solutions. **A**, Baseline (no immersion). **B**, pH 2 buffer only. **C**, pH 7 buffer only. **D**, pH 10 buffer only. **E**, Three cycles of 9-day cycling of pH 2, 7, and 10 sequence (3-day immersion per buffer). **F**, Three cycles of 9-day cycling of pH 10, 2, and 7 sequence (3-day immersion per buffer). (From Esquivel-Upshaw JF, Ren F, Hsu SM, et al: Novel testing for corrosion of glass-ceramics for dental applications, *J Dent Res* 97:296–302, 2018. doi:10.1177/0022034517732283. Epub 2017 Sep 18. PubMed PMID: 28922616; PubMed Central PMCID: PMC5833181, with permission.)

The International Organization for Standardization (ISO) is an independent, nongovernmental international organization that develops specifications for products and services to ensure quality, safety, and efficiency. The ISO/Technical Committee 106 (TC 106) was specifically designed to develop standards for dental materials testing. Unfortunately, dental manufacturers' adherence to ISO standards is desirable but not required. Additionally, most of these in vitro tests cannot be correlated with what occurs in the oral environment. For example, the ISO 14569 for wear of enamel and a dental material is measured using a pin-on-disk system. The setup is that one material is in the form of a disk or a pin and the opposing material (preferably enamel) is on the other end. Both materials are rotating in a circular motion on a flat plane. The reality is that teeth are not flat, and the temporomandibular joint functions on an arch and then a slide to produce a complex movement along cuspal inclines and fossae. So, the wear of a dental material as measured by these standards cannot reasonably be correlated with clinical performance.

Another example is the test for the chemical durability of ceramic materials (ISO 6872:2015), which is conducted by immersing the ceramic in a pH 2.4 buffer solution at 80 °C for 16 hours. This scenario does not represent the oral environment in that the diet of each individual exposes the material to a myriad of pH changes. In addition, the buffering capacity of saliva continually strives to neutralize this environment to pH 7.4, so there is a constant fluctuation of pH in the oral cavity. A recent in vitro study introduced the concept of pH cycling, where glass-ceramic disks were exposed to a sequence of pH 2, 7, and 10 buffer solutions over a period of 27 days at 80 °C. The effects of immersion in buffer solutions on the surface of ceramic specimens are shown in Figure 19-1. This study demonstrated that the surface degradation and material loss was significantly greater

during the pH-cycling testing methodology than the constant immersion currently being employed as a standard test. The study proposes that two dissolution mechanisms work synergistically when the pH is cycled. In an acidic solution, an ionic exchange mechanism occurs where the network modifiers (Al, Ca, K, Zn) are exchanged for the ions in solution. This leaves a weakened corrosive layer on the surface. In a basic solution, a total dissolution process occurs where the Si-O bonds are cleaved, and the surface layer is corroded. In a constant-immersion environment, a steady state is reached where no further corrosion occurs. However, in a pH-cycled environment, alternating between acid and base, the basic solution will attack not only the Si-O bonds but also the corroded layer produced by immersion in an acidic environment. Thus there is a constant dissolution process that is corroding the surface of ceramic. Although the pH cycling test represents extremes in the oral environment, this method suggests that the current standard of constant immersion could be underestimating the potential for surface degradation of materials in the mouth. Therefore in vitro testing is ranked as the lowest form of evidence by EBD standards.

CRITICAL QUESTION

What is the best type of clinical study and why?

Observational Studies

In vivo observations are the second tier of dental evidence as classified by EBD. These types of studies include retrospective studies, prospective studies, case-control studies, and cohort studies. The dental literature is replete with observational studies that examine the performance of dental materials over time.

Retrospective Studies

Retrospective studies look back in time for applied interventions and examine the outcome in the present time. For example, a retrospective analysis can be performed on the longevity of the types of post and core materials by performing a chart review, categorizing the types of materials used, and evaluating the duration these post and cores were in service intraorally. The advantages of these studies are that data are readily available to be analyzed, and they are relatively inexpensive to execute. The disadvantages include no standardization of placement of these materials because there are multiple operators involved, records may be incomplete, and the presence of multiple variables is very difficult to ascertain. Statistically, there is a higher chance of error with these types of studies, resulting from confounding variables and bias.

Case-Control Studies

Case-control studies are also observational studies and are generally retrospective. These studies have an outcome status and an exposure status that are not determined by the investigator. This type of study will generally examine two groups, one with and one without the outcome, to determine whether there is an exposure and try to infer causation. An example of this could be the neurological effects of dental amalgam where investigators identify groups with an outcome (neurological defects) and an exposure status (presence of amalgam in their mouths) and try to find an association. As with retrospective studies, these are relatively inexpensive, although they provide less evidence for causation.

Prospective Studies

Prospective studies can be observational or controlled and randomized, and they are planned longitudinal experiments—for example, a study comparing the wear of enamel against metal-ceramic crowns and all-ceramic crowns. These two groups (or cohorts) can be followed over a specified duration of time to determine which material is more wear-friendly to enamel. These studies are more expensive because they have to be planned, and participants must be followed for long periods of time.

Randomized Controlled Clinical Trials

RCTs are considered the gold standard of evidence-based sciences. These studies randomize the allocation of participants into groups to minimize bias and confounding variables and are controlled, meaning there is the presence of a control group where participants receive no treatment or the current standard of treatment. These studies are prospective and longitudinal, which is one of the reasons they are not very common because they are expensive and logistically very difficult to conduct. An example of an RCT is comparing the survival of metal-ceramic crowns and ceramic-ceramic crowns in three-unit fixed dental prosthesis. The metal-ceramic material serves as the control or the standard of care. The objective is to determine whether there are advantages to the new material over the old material and whether these outweigh the disadvantages.

CRITICAL QUESTION

What are the factors that would limit interventions applied in a clinical study?

Clinical Analysis of Survival and Acceptability

As mentioned earlier, the best form of evidence is clinical performance studies, either as observational studies or randomized and controlled interventional studies. Because human experiments are

well controlled and regulated by ethical boards, intervention has to fall within a reasonable benefit-to-risk ratio. In other words, the risks for conducting the study should not outweigh the benefits, and no harm should be promoted in the experiment. For this reason, clinical studies are limited to mostly observation of occurrences. For example, a crack cannot purposely be introduced into a ceramic crown and cemented onto a patient's mouth to enable observation of the phenomena of progression of slow crack growth in vivo. Similarly, a biopsy of a healthy peri-implant site cannot be performed for the sole purpose of being able to compare bacterial flora to a diseased peri-implant site. This section will describe several in vivo measurements that are currently being employed to assess the clinical performance of dental materials. First is a description of how restorations are being assessed after periodic performance intraorally. Second are two methods of measuring and quantifying wear in vivo. Third is a forensic assessment of clinical fractures through fractographic analysis.

CRITICAL QUESTION

What is the rationale for calibrating evaluators in a clinical study, and why is there a need for dual evaluation?

Clinical Assessment of Restorations

Perhaps the oldest and most important clinical assessment tool is the rating scale published by Cvar and Ryge in 1971 in the U.S. Public Health Service Guidelines (USPHS; [Box 19-1](#)). The original parameters used for evaluating dental restorations were color match, marginal discoloration, marginal integrity, anatomical form, and the presence of dental caries. The parameters were graded alpha (A), bravo (B), and charlie (C). These rankings were created to differentiate restorations that were within the range of excellent, acceptable, needing future replacement to prevent damage, and needing immediate replacement. The key to the success of this grading scale is the systematic calibration of the reviewers to ensure that (1) the evaluators are familiar with the grading scale, (2) they possess the visual discrimination for assessment, and (3) they maintain consistency in grading longitudinal studies. Another requirement is the implementation of dual evaluators and a process by which they can resolve differences in grading. The original study noted that the accuracy of a trained and calibrated evaluator is about 85%. The inclusion of a second trained and calibrated evaluator increases the accuracy of the rating to 98%. One aspect of this study that was never really implemented is the universal collection of photographs and study models to enable calibration across clinical studies. With time, modified versions of the clinical assessment tool have come to include additional parameters, such as occlusion, postoperative sensitivity, fracture, retention, and others, depending on the needs of the study and the restoration being evaluated. Perhaps the biggest obstacle to clinical studies is cost, which largely explains why most studies have no controls and only one evaluator.

In 2007, the Fédération Dentaire Internationale (FDI) released its own version of the clinical assessment of restorations. The FDI subdivided the different parameters according to esthetic, functional, and biological groups ([Box 19-2](#)) for a total of 16 parameters in all. The grading scale was expanded to include clinically excellent, clinically good, clinically satisfactory, clinically unsatisfactory, and clinically poor. To facilitate calibration between multiple sites, the FDI also posted an online calibration guide, but this, of course, is no replacement for the hands-on clinical

• BOX 19.1 Original Cvar and Ryge Criteria Used to Evaluate Restorations

Color Match

Oscar (O)	Anterior restoration, invisible without a mirror
Alfa (A)	Posterior restoration, matching the adjacent tooth in color, shade, and translucency
Bravo (B)	Posterior restoration; the mismatch in color, shade, and translucency between the restoration and the adjacent tooth within normal range
Charlie (C)	Posterior restoration; the mismatch in color, shade, and translucency between the restoration and the adjacent tooth outside normal range

Cavo-Surface Marginal Discoloration

Alfa (A)	No discoloration anywhere on the margin between the restoration and the tooth
Bravo (B)	Discoloration present but does not penetrate along the margin toward the pulp
Charlie (C)	Discoloration present and penetrates along the margin toward the pulp

Anatomical Form

Alfa (A)	Restoration continuous with existing anatomical form
Bravo (B)	Restoration undercontoured, i.e., discontinuous with existing anatomical form but dentin/base not exposed
Charlie (C)	Restoration undercontoured, i.e., discontinuous with existing anatomical form and dentin/base exposed

Marginal Adaption

Alfa (A)	No visible evidence of a crevice along the margin into which an explorer penetrates
Bravo (B)	Visible evidence of a crevice along the margin into which an explorer penetrates but dentin/base not exposed
Charlie (C)	Visible crevice along the margin with exposed dentin/base; the restoration is not mobile, fractured, or missing in part of the tooth
Delta (D)	Restoration mobile, fractured, or missing in part of the tooth

Caries

Alfa (A)	Caries absent along the restoration margin
Bravo (B)	Caries present along the restoration margin

calibration that occurs. As with the USPHS scale, investigators are able to tailor the criteria based on their studies and needs.

CRITICAL QUESTION

What qualities of wear are desirable in a dental material?

• BOX 19.2 Fédération Dentaire Internationale (FDI) Revised Criteria for Evaluating Clinical Restorations

Esthetic Criteria

Surface luster
Staining: (a) surface and (b) margin
Color match and translucency
Esthetic anatomical form

Functional Criteria

Fracture of material and retention
Marginal adaptation
Occlusal contour and wear
Approximal anatomical form: (a) contact point and (b) contour
Radiographic examination, where applicable
Patient's view

Biological Criteria

Postoperative sensitivity and tooth vitality
Recurrence of caries, erosion, abfraction
Tooth integrity
Periodontal response
Adjacent mucosa
Oral and general health

For all three groups, the following gradings are used for evaluation:

Clinically excellent/very good
Clinically good
Clinically sufficient/satisfactory
Clinically unsatisfactory
Clinically poor

Wear Analysis

One of the most important criteria for dental materials is durability and compatibility with opposing structures. These two parameters are clearly measured through wear analysis, in that these materials must be durable enough to withstand occlusal forces by not wearing away and at the same time exhibiting comparable wear of opposing enamel. Wear of restorative material surfaces can cause damage to the opposing structures. A worn surface usually translates into a roughened surface, which can encourage plaque accumulation, caries formation, and wear of the opposing tooth surface. Consequently, worn surfaces can result in a decrease in the occlusal vertical dimension, which could then lead to occlusal trauma, periodontal disease, and temporomandibular joint dysfunction. As mentioned earlier, the standard test for wear is not representative of occlusal function. Several wear machines or chewing simulators were developed that introduced varying load, vertical and horizontal movement, and thermocycling. However, none of these chewing simulators was found to correlate well with clinical scenarios. Therefore the best measure is to determine the wear of enamel and dental materials in a clinical setting. There are two ways to quantify clinical wear: indirect and direct.

Indirect Method

The indirect method is the most commonly used method for measuring clinical wear. The method is indirect because replicas are made using an elastomeric impression of the area of interest (dental material and/or opposing tooth enamel), and stone models are made where the measurements are conducted. The measuring

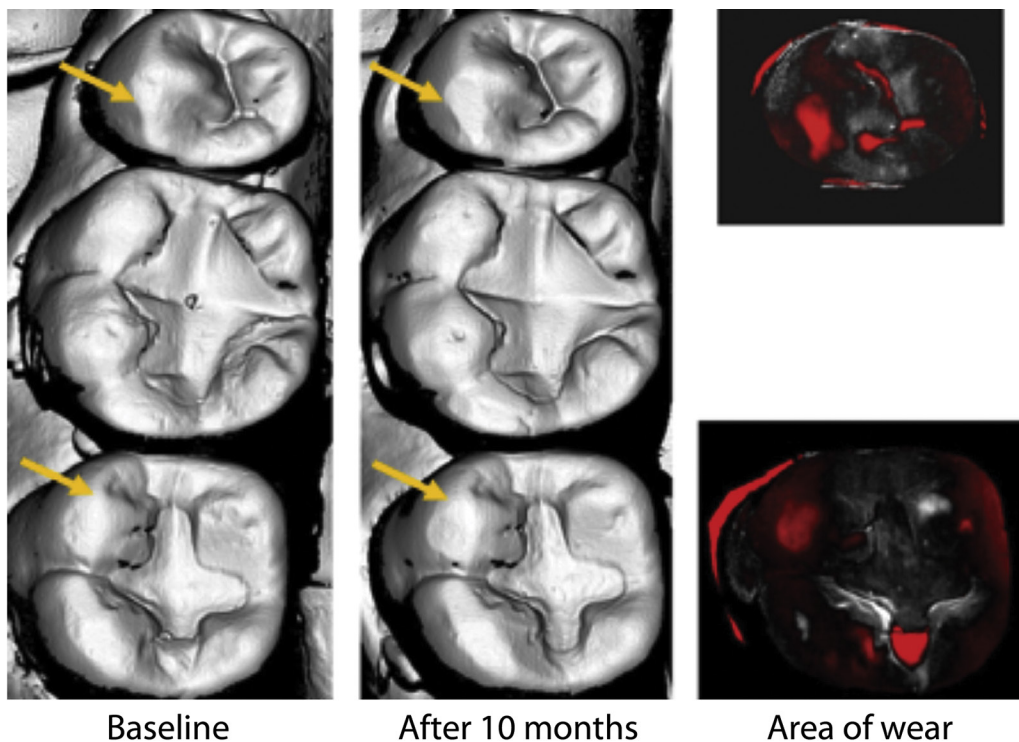
devices are diverse and can include laser scanners, micro-computed tomography (micro-CT), or surface profilometers.

A laser scanner produces a three-dimensional (3-D) image through the movement of an object (in this case, a tooth replica) under the projection of a laser beam. The reflection of the cross-section profile of the object is detected by sensors, which produces an image consisting of “point clouds.” Each point represents x-, y-, and z-coordinates on the scanned surface. Each profile can then be combined and transformed into high-resolution images through advanced software that allows for comparison and measurement. The edge effect is an error or artifact that is produced when the laser beam hits a sharp edge or the bottom of a groove, producing overshoot reflections. Laser beam measurements are also affected by surface reflections of the material being scanned, so stone or elastomeric impression materials are used as replicates to minimize these reflections.

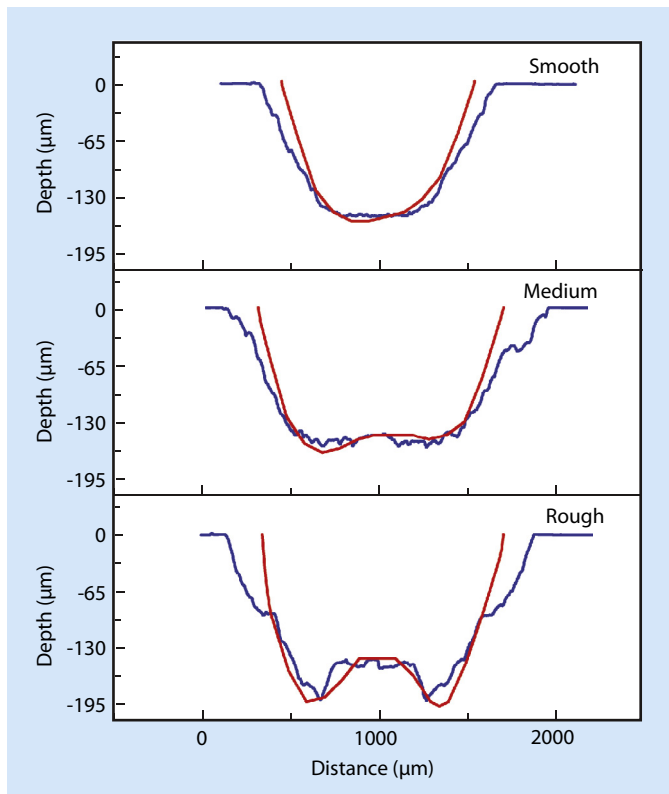
Laser scanners can either have red or blue laser beams. Higher-wavelength beams (red beams) have lower resolution, more diffraction, and less intensity compared with the blue laser beams. Depending on the nature of the material being scanned, the laser can penetrate through the material to cause a diffusion on the surface, which can result in a loss of focus on the surface being measured and sends inaccurate readings back to the detector, which in turn leads to invalid measurements.

When measuring the clinical wear of a dental material, a baseline impression and a replica model of the teeth involved in the measurement are first made. Depending on the study protocol, an impression and replica are once again produced during the designated follow-up time, either in months or years. The wear that occurred between baseline and the period of interest are measured using specialized scanners with software that can superimpose images by using known landmarks and calculating volume loss and maximum wear

depth. **Figure 19-2** demonstrates teeth-opposing ceramic crowns that were monitored for 10 months. Baseline and period replicas are shown on the left, with yellow arrows pointing to areas that are worn. A laser scanner device was used to superimpose the two replicas. The image on the right demonstrates red areas that highlight the areas on the teeth where wear occurred. The maximum wear or the maximum-wear depth value is perhaps more important than calculating the volume loss of a material. Volumetric wear can occur over a large surface area and therefore not be detrimental to the integrity of the tooth or the restoration if the depth is shallow and remains superficial. However, maximum wear indicates maximum depth, which can prove to be more damaging. For example, when calculating the wear of enamel, if volume loss is large but occurs over a wide area, the wear can be limited to enamel. However, if the maximum wear refers to depth and the value is large, then there is a possibility of wear through the dentin. There are several laser scanners available on the market that are used for quantifying wear. Unfortunately, the validity of these measurements is rarely verified with calibrated instruments such as micro-CT or a profilometer. As mentioned earlier, there are errors that can be produced from the laser-scanning process. **Figure 19-3** demonstrates the discrepancies between a laser scanner and surface profilometer in measuring the depth profile of indentations produced by different-grit diamond burs on a ceramic surface to simulate wear. This in vitro study evaluated the validity of a red laser scanner in measuring depth and volume against a surface profilometer, in addition to the effect of bur grit on these measurements. Gross over- and underestimations of depth and volume wear measurements were observed with the laser scanner compared with the surface profilometer. These errors probably resulted from a combination of the edge effect mentioned previously, the nature of the material being scanned, and the high



• **Figure 19-2** Wear areas (yellow arrows) on teeth noted after 10 months of service on teeth opposing an all-ceramic fixed dental prosthesis. Comparison software on the far right reveals red areas indicating where wear occurred. (From Esquivel-Upshaw JF, Young H, Jones J, et al: In vivo wear of enamel by a lithium-disilicate core ceramic used for posterior FPDs: First-year result, *Int J Prosthodont* 19:391–396, 2006.)

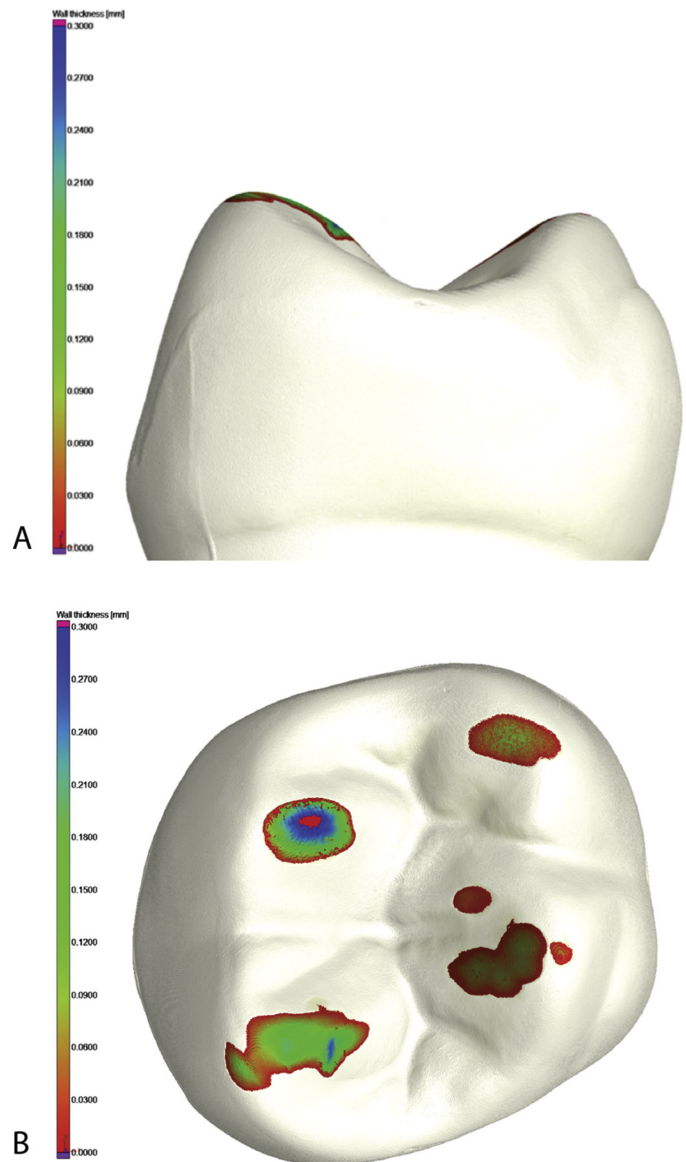


• **Figure 19-3** Depth-profile comparison between laser scanner (red) and profilometer (blue) indicating major differences in depth and width of indentations caused by different-grit diamond burs. Edge effect, artifact, and surface reflectance could be partially responsible for the inaccuracies. (From Hsu SM, Ren F, Abdulhameed N, et al: Comprehensive analysis of laserscanner validity used for measurement of wear, *J Oral Rehabil* 46:503–510, 2019.)

wavelength of the beams. Nonetheless, although laser scanners are a convenient tool for measuring clinical wear, the users have to be judicious in determining the accuracy and the validity of the wear measurements.

Micro-CT can also be used to measure clinical wear using the indirect method. Micro-CT uses x-rays to see through an object slice by slice. These two-dimensional (2-D) images are then rendered through a software program to produce a 3-D model of the object or analyzed in cross-sections. For the purpose of wear analysis, wear can be quantified through analysis of the replicas. Figure 19-4 demonstrates the mesial and occlusal views of a dentoform tooth that has been placed in a chewing simulator to receive random wear at multiple sites. The micro-CT was used to scan the tooth before and after wear occurred, and the results are shown in Figure 19-4, where the colored areas refer to the areas of wear, which are quantified according to the grid shown on the side.

Surface profilometry can also be used for quantitative wear evaluation using the indirect technique. The contact profilometer has a stylus that traverses the surface of the object being measured, whereas the noncontact profilometer uses a laser beam or white light to probe the surface. The contact stylus is usually a metal or diamond ranging from 2 to 20 μm in diameter loaded with a contact load of few millinewtons while contacting the surface. The scan can provide a map of the surface topography. Although this method is considered precise for depth profilometry, the process is time consuming. For this type of measuring device to be effective,

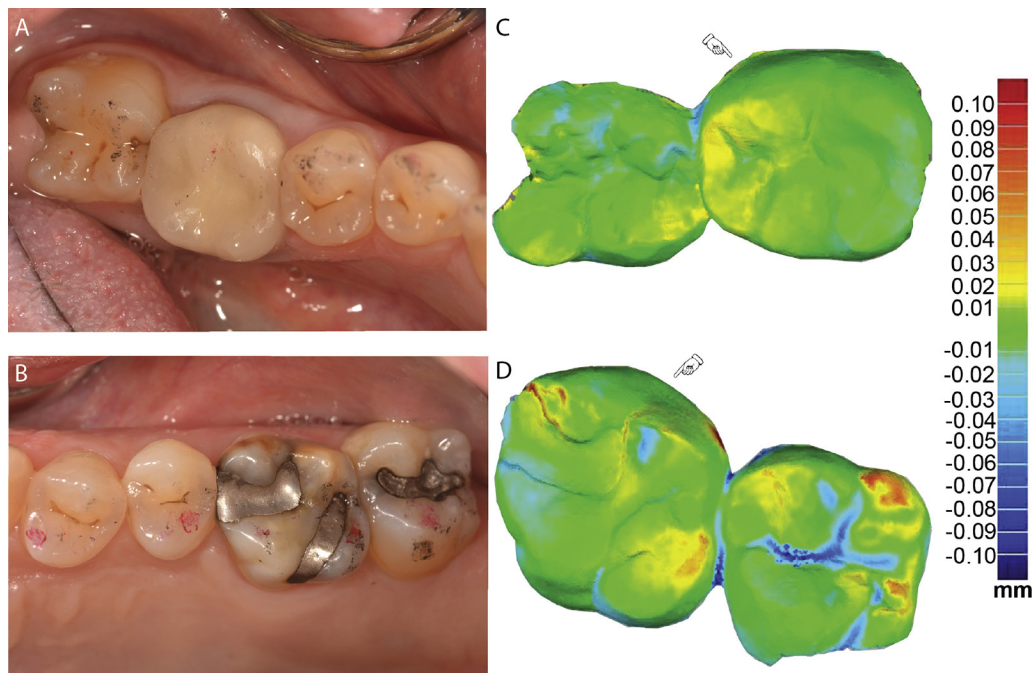


• **Figure 19-4** Three-dimensional reconstructed image from micro-CT scan of a dentoform tooth demonstrating wear. **A**, Mesial (or distal) aspect. **B**, Occlusal surface. The color bar to the side reflects wear depth in millimeters. (From Esquivel-Upshaw JF, Hsu SM, Bohórquez A, et al: Novel methodology for measuring intraoral wear in enamel and dental restorative materials, *Clin Exp Dent Res* 8:1–9, 2020, doi:10.1002/cre2.322. PubMed PMID: 32955159; with permission.)

reference points need to be placed on the teeth of interest to orient the user to the exact area being measured.

Direct Method

With the advent of digital impressions, this method uses the technology of intraoral scanning to allow quantitative wear measurement. The teeth to be measured are scanned at baseline and then again at periods of interest. These scans are then compared using comparison software that essentially superimposes both images and identifies the differences in depth and volume between the two. The process of intraoral scanning is technique sensitive. Some intraoral scanners use a powder spray of zinc oxide to minimize the reflection of enamel during the scanning process. The area being scanned has to be completely isolated so



• **Figure 19-5** Direct method of wear measurement using intraoral scanner. **A**, A ceramic crown on mandibular left first molar. **B**, Opposing left maxillary quadrant. **C**, The result of superimposing baseline and 1-year scan to quantify the wear that occurred on the ceramic crown (*pointer*) by the comparison software using the adjacent second molar as the enamel control. The color bar to the side reflects wear depth on the ceramic restoration and the enamel control in millimeters. **D**, The result of opposing maxillary first molar. (From Esquivel-Upshaw JF, Hsu SM, Bohórquez A, et al: Novel methodology for measuring intraoral wear in enamel and dental restorative materials, *Clin Exp Dent Res* 8:1–9, 2020. doi:10.1002/cre2.322. PubMed PMID: 32955159; with permission.)

that saliva does not mix with the powder. The powdery sludge can become thick and cause an error in the scanning process. There is also the steep learning curve associated with operating the software. The scanned images have to be adeptly cropped to minimize noise in the superimposition. Figure 19-5 is an example of the direct method. Figure 19-5, *A & B* depict clinical images of two opposing quadrants, with the crown on the mandibular left molar being the area of interest and the opposing tooth on the maxillary. These teeth were scanned at baseline and then again at 6 months, and the images (Figure 19-5, *C & D*) demonstrate the amount of wear (color grid in millimeters) during this period of time. Although this is perhaps the most convenient and expedient method for quantifying wear, the technical sensitivity and the errors that could be associated with scanners have to be considered.

CRITICAL QUESTION

What forensic information can we ascertain from fractographic analyses?

Critical Observation and Fractographic Analysis

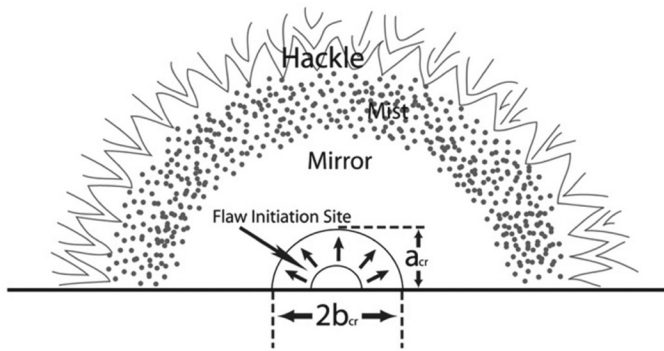
A fractured restoration can fall under the modified version of the USPHS under functional criteria. However, fracture surfaces often reveal information about how and why the fracture occurred. That is why the critical observation and analysis of fractures deserves a separate section in this chapter.

Characteristics of Fracture Surface

Fractography is the study of the fracture surfaces of materials. Through characteristics visible on the surface of these fractures, the origin of the fracture, the load and orientation of the fracture, and the progression of the failure can be determined for the particular material. There have been significant advances in the application of fractography to the understanding of fracture mechanics. Several works have identified the key parameters that are important to the understanding of why fractures occur. When a material fractures in a brittle manner, the fracture surface records the event in such a way that many important features are made clear. A schematic diagram of a typical crack in glass or ceramic is depicted in Figure 19-6. Some very prominent features of these cracks are the origin, mirror, mist, and hackle. These features, when visible by magnification, can usually give an indication as to the propagation direction of the fracture. The presence of any residual stresses can be determined from the fractured area and the stress at which fractures occur, which can be measured from the crack size.

Almost all mechanically induced cracks can be idealized as a semielliptical, sharp crack with depth, a , and width, $2b$ (Figure 19-6). Recall the discussion of the Griffith energy approach to fracture and the following equation (Chapter 4, Fracture Toughness):

$$K_{Ic} = Y\sigma_f\sqrt{c} = \sqrt{2E\gamma_c}, \quad (1)$$



• **Figure 19-6** Schematic diagram of crack in a brittle material with the critical flaw size and the different features that can enable calculation of stress and the direction of fracture.

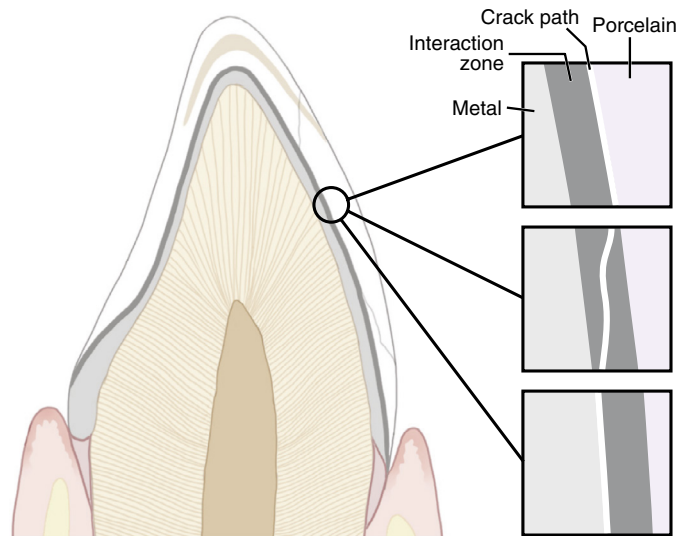
where K_{Ic} is the critical stress intensity factor (fracture toughness), Y is a geometrical factor that accounts for the shape of the fracture-initiating crack, E is the elastic (Young's) modulus, c is the radius of an equivalent semicircular or semielliptical crack ($c = \sqrt{ab}$), and γ_c is the critical fracture energy (i.e., all the energy involved in fracture, including the creation of new surfaces). The small semiellipse in Figure 19-6 represents the initial flaw size, and the large semiellipse is the critical flaw size that leads to fracture. Because the value of K_{Ic} can be obtained from testing standardized specimens, the level of stress causing the fracture can be calculated by the measurement of equivalent semielliptical crack, c . For further information on the process involved with fractographic analysis, the reader is referred to the fractographic books and articles mentioned at the end of this chapter.

Clinical fractures of metal-ceramic restorations, although rare, still occur, especially when a new alloy or veneering porcelain is being used or when a new technology has been adopted. As is generally true for all dental materials, there is a learning curve associated with the initial use of new products. Although there is an infinite number of fracture paths that may occur, three types are of particular importance in diagnosing the cause of fracture. Figure 19-7 shows the fracture paths that have occurred primarily at three sites in a metal-ceramic crown: (1) along the interfacial region between opaque porcelain (P) and the bonding zone (I) between porcelain and the metal substrate (top), (2) within the bonding zone (center), and (3) between the metal and the bonding zone (bottom). For conventional metal-ceramic crowns made from cast copings, the bonding zone is synonymous with the metal oxide layer.

Characterization of Fracture Surface

To characterize the principal site of fracture, a low-magnification examination of the fracture surface may be sufficient in a few cases. However, a magnification of 3 to 100 times is more often required because minute microstructural details such as pores may reveal wake-hackle patterns that clearly show the direction of crack propagation in these areas. Fractographers seek important crack features, such as hackle, twist hackle, wake hackle, arrest lines, and compression curl, to lead them toward the critical flaw or source of crack initiation and the possibility of identifying one or more mechanisms of failure.

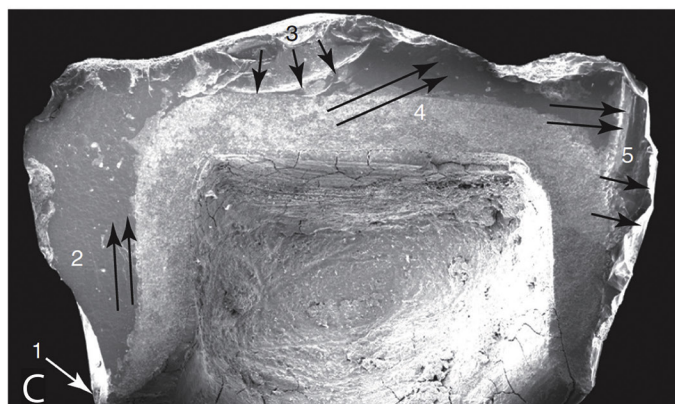
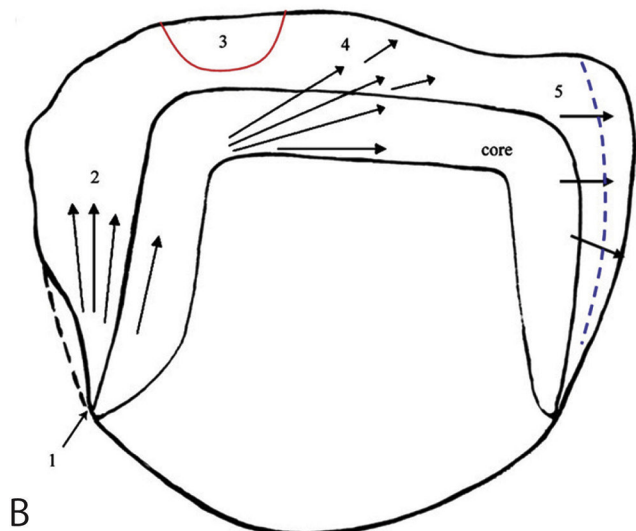
Each of the three principal fracture paths in Figure 19-7 is indicative of excessive tensile stress, a material defect, or a processing factor. The location and appearance of a fracture sur-



• **Figure 19-7** Cross-sectional illustration of three principal types of interfacial zone fracture in a metal-ceramic crown.

face are major factors used to determine the cause of fracture. For fractures that are confined to the occlusal surface of posterior crowns, a cone-crack type of fracture (apex of the cone at the fracture surface and the base of the cone extending into the veneer) suggests that localized loading at small contact areas may be the cause. Fractures that occur in the proximal occlusal area of the crowns may be caused by inadequate support of the veneer by the core framework material. Fractures that occur well away from the sites of loading may be caused by thermal incompatibility stresses. The procedures for obtaining evidence from fractured all-ceramic restorations are the same as those used for metal-ceramic restorations.

When fractures occur, making a vinyl polysiloxane impression of the fracture site as soon as possible is useful for future fractographic analysis. All information on the crown or bridge should be recorded, including the visual appearance of the fracture site. A photograph is also very helpful in analyzing the potential cause of fracture. The impression allows a replica of the fracture surface to be made from epoxy resin. The replica allows fractographic observations of the fracture surface to be made, and these models can then be examined by a fractography expert under low magnification using optical microscopy and stereomicroscopy, followed by scanning electron microscopy (SEM). The location of the critical flaw indicates the origin of the fracture. Fracture surface markings observed on the replica assist the expert in determining the origin and confirming the suspected cause of fracture. Shown in Figure 19-8, A is a residual section of a fractured Procera AllCeram alumina-based crown with a glass-phase veneer that fractured after 4 years of clinical service. The cause of fracture can be assessed by visual inspection, characterization of principal fracture features, detailed examination of optical microscopy and stereomicroscopy images, and if necessary, SEM images. The stereomicroscopic analyses of the retrieved fractured segment revealed the fracture paths that are shown in Figure 19-8, B. They include crack initiation (areas 1 and 3), crack propagation (areas 2 and 4), and completion of fracture (area 5). Area 3 illustrates the initiation of a cone crack that could have led to cone-type fracture discussed earlier but did not propagate far enough to cause the bulk fracture. This fracture analysis illustrates incidental surface damage in



• **Figure 19-8** Analysis of a fractured restoration. **A**, Fractured Procera AllCeram premolar crown. **B**, Sketch of key findings after stereomicroscopic analyses of the retrieved fractured segment. The initiating crack occurred at the mesial margin (area 1) and propagated upward approximately 2 mm before crown fracture occurred in areas 2 and 4, terminating in the compression curl area 5. Area 3 represents contact damage within the occlusal veneering ceramic that does not extend into the alumina core ceramic. **C**, Confirmation of the finding by scanning electron microscope image. (From Scherrer SS, Quinn GD, Quinn JB: Fractographic failure analysis of a Procera® AllCeram crown, *Dent Mater* 24:1107–1113, 2008.)

an area where crack propagation was localized only in the veneer ceramic. **Figure 19-8, C** is the confirmation of five fracture surface features in the sketch by the SEM image. This forensic analysis of how the fracture progressed was made possible by the different landmarks that are prominent on fractured brittle surfaces.



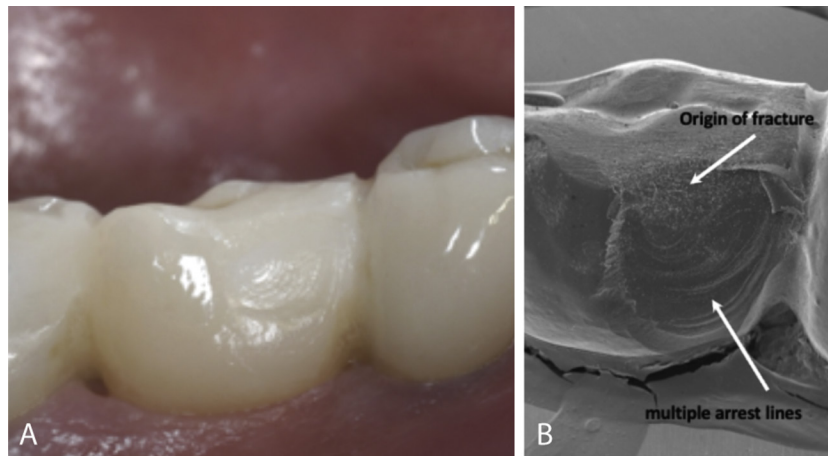
• **Figure 19-9** Inspection for cracks using fiberoptic transillumination prior to cementation is important in improving the predictability of ceramic crowns.

The fractographic procedures described previously are based on the assumption that the prosthesis was free of cracks during try-in and during cementation. However, dentists are not typically trained to inspect prostheses received from the lab using fiberoptic transillumination. Examination under such lighting can reveal surface and subsurface cracks that may exist in the ceramic and metal-ceramic prostheses either before or after try-in for fit. **Figure 19-9** shows a laboratory technician who is using a fiberoptic light source to inspect a ceramic prosthesis for cracks that may be hidden from typical fluorescent or incandescent light sources.

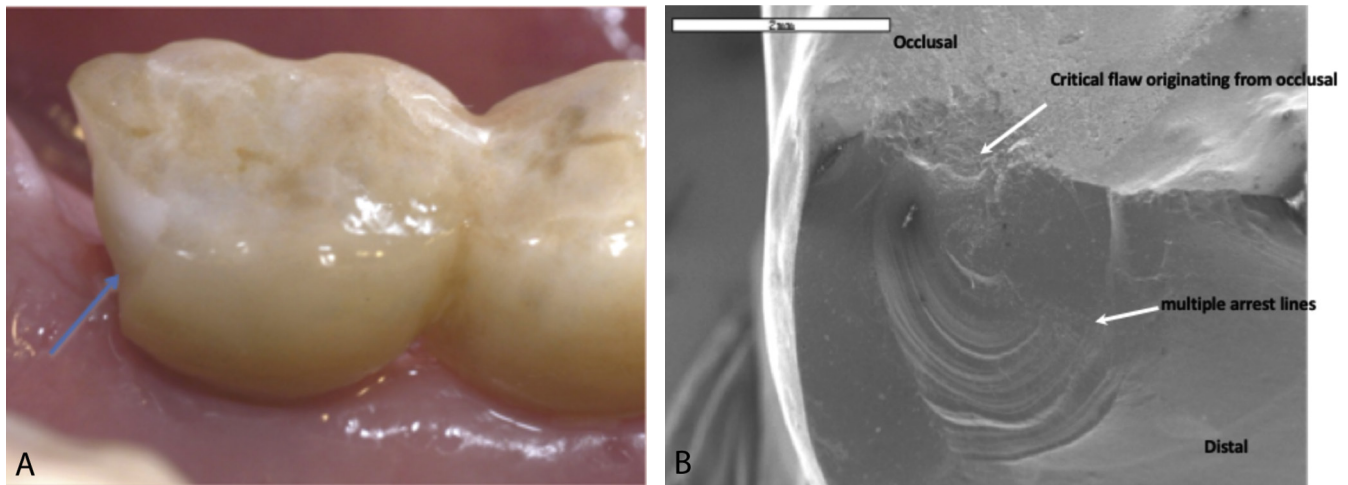
Many factors are associated with the fracture of all-ceramic prostheses. These factors fall into one of eight categories: (1) inherent surface defects, (2) processing defects, (3) loading (bite force and load orientation), (4) design, (5) material properties, (6) residual stress, (7) procedural errors, and (8) diet. Within these categories, the following variables may contribute to crack initiation, crack propagation, chipping, and bulk fracture: surface treatment, excessive loading during try-in, bruxing loads, loading location, load distribution, load magnitude, transient cooling stresses, residual cooling stresses, inadequate tooth preparation, improper core framework design, inadequate crown thickness, inadequate core thickness, improper connector size, quality of the cement layer, bond quality of ceramic veneer to ceramic, voids in the cement layer or at the cement/ceramic interface, and the elastic moduli of component and supporting substrate materials. To reduce the risk for ceramic fracture, sufficient tooth reduction, sufficient thickness of the ceramic, adequate prosthesis design, distributed vertical loading, and meticulous attention to the recommended manufacturers' procedures are required.

Classification of Ceramic Restoration Fractures

Grading fractures of ceramic restorations has been recommended and is based loosely on the original USPHS criteria for grading restorations. Heinze and Rousson introduced the classification in 2010, with Class 1 being minor, no intervention required; Class 2, repair was needed; and Class 3, replacement was required. **Figures 19-10** to **19-12** illustrate three clinical scenarios of what these classes look like clinically. **Figure 19-10, A** shows a veneered zirconia crown with a class 1 lingual fracture. The fracture was small enough that even the patient did not know there was anything



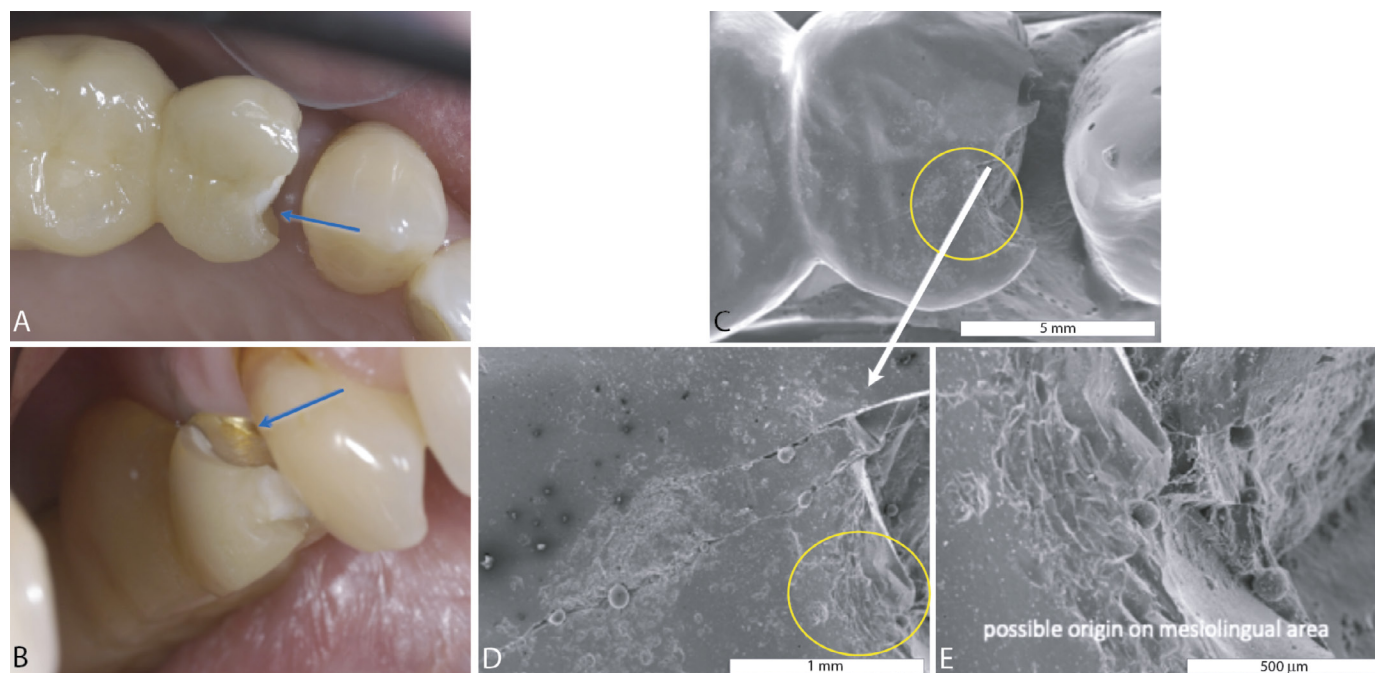
• **Figure 19-10** Class 1 fracture. **A**, Minor fracture on the lingual side of a ceramic-ceramic crown; no intervention required. **B**, Scanning electron microscope identifies the fracture origin (arrow) on the occlusal surface and propagated gingivally, as shown by multiple arrest lines (arrow). (From Esquivel-Upshaw JF, Mecholsky JJ Jr, Clark AE, et al: Factors influencing the survival of implant-supported ceramic-ceramic prostheses: A randomized, controlled clinical trial, *J Dent* X3:100017, 2020; with permission.)



• **Figure 19-11** Class 2 fracture. **A**, Fracture at distal edge (arrow) of a veneered zirconia; repair needed. **B**, Fractographic analysis identifies the critical flaw on the occlusal surface of the restoration. (From Esquivel-Upshaw JF, Mecholsky JJ Jr, Clark AE, et al: Factors influencing the survival of implant-supported ceramic-ceramic prostheses: A randomized, controlled clinical trial, *J Dent* X3:100017, 2020, with permission.)

wrong. SEM analysis (Figure 19-10, B) reveals the origin of the fracture to be on the occlusal surface of the crown. Figure 19-11, A is a class 2 fracture of a veneered zirconia crown on the distal edge. Although the indication is to have this repaired because the fractured surface is substantial, these repairs made with composite resin and a silanating agent usually fail within a couple of years. Fractographic analysis (Figure 19-11, B) revealed that the fracture also originated from the occlusal surface of the prosthesis. Figure 19-12, A & B is a class 3 fracture, also of a veneered zirconia crown. The fracture went through the veneer and fractured the core substructure. However, fractographic analysis (Figure 19-12, C-E) revealed that the fracture originated from the occlusal surface and propagated through a series of multiple fractures.

In summary, the performance of dental materials is best determined through clinical trials and observations because there are no in vitro tests that mimic the oral environment. However, there are limits to what can be measured intraorally, and interventions have to be ethical. The contributing factors to failure are very difficult to ascertain without performing a systematic forensic analysis (such as in fractography). The biggest drawback is that these clinical tests, if done properly, are expensive and very time consuming. By the time the results are released for a poorly performing material, the manufacturers might have already moved on to the promotion of another discovery. Thus the feedback that should be gleaned to improve the next generation of materials is lost.



• **Figure 19-12** Class 3 fracture. **A**, Occlusal view of a fractured veneered zirconia; needs replacement. **B**, Mesial-facial view showing fracture through the zirconia core. **C–E**, Series of fractographic analysis demonstrates multiple fractures that propagated from one on the occlusal surface. Circles indicate the area expanded in the succeeding images. (From Esquivel-Upshaw JF, Clark AE, Shuster J, et al: Factors influencing the survival of implant-supported ceramic-ceramic prostheses: A randomized, controlled clinical trial, *J Dent* X3:100017, 2020, with permission.)

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Full Selected Readings for this chapter can be found on www.expertconsult.com.

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20

Emerging Technologies

OUTLINE

Biomaterials

Biological Materials

Instruments and Processes

Summary

KEY TERMS

Bioactive Having an effect on or eliciting a response from living tissue, an organism, or a cell, especially in inducing the formation of superficial hydroxyapatite.

Bioinductive Capable of inducing a response in a biological system.

Biomaterial Any matter, surface, or construct that interacts with biological systems.

Biomimetics Study of the formation, structure, or function of biologically produced substances and materials (e.g., silk or nacre) and biological mechanisms and processes (e.g., protein synthesis or mineralization) for the purpose of synthesizing similar products by artificial mechanisms that mimic natural structures.

CAD-CAM CAD refers to computer-aided design technology, based on the use of computer software and systems to assist in the creation, modification, analysis, and optimization of two-dimensional or three-dimensional models of objects. Any computer program that embodies computer graphics and an application program that facilitates engineering functions in the design process can be classified as CAD software. The term CAM refers to computer-aided manufacturing of a restorative device using the CAD input file. CAM may be additive (buildup) or subtractive (machining of a device from a larger starting piece of material).

Cytology The harvesting of disaggregated cells and related microscopic material for analysis of disease.

Nanotechnology Technology that focuses on the atomic and molecular scale (<100 nm) of materials, devices, and other structures. On this scale, in which at least one dimension must be below 100 nm, quantum mechanics (quantum theory) controls material properties or behavior.

Osteoconductive Capable of acting as a matrix or scaffold to facilitate new bone growth on its surface.

Self-assembling materials Disordered materials that form an organized structure or pattern as a consequence of specific, local interactions among the components, without external direction.

Smart materials Synthetic materials that interact with external stimuli, such as light, temperature, stress, moisture, pH, and electric/magnetic fields, in such a way as to alter specific properties in a controlled fashion and return to the original state after the stimulus has been removed.

Voxel Volumetric picture element that represents a single sample, or data point, on a regularly spaced three-dimensional grid. It is analogous to how *pixel* defines a point in two-dimensional space.

The materials and devices in current use are effective, but improvements in performance are always needed. For instance, caries-prevention treatments have reduced the need for initial restorations, replacement restorations, and removable dentures. Minimally invasive dentistry concepts have led to the removal of less tooth structure and the sealing of leaking defective margins of restorations. Nonetheless, because of the promotion of higher-cost esthetic restorations, sometimes at the expense of durability, the need for both repair and replacement of restorations will continue because resin restorative materials fail and degrade over time. Thus the choice of materials for a given clinical situation will continue to be based on a comparative analysis that balances cost, benefits, and risks. Until caries is considered truly “curable,” there will be a need for novel solutions, such as remineralizing agents, **smart materials**, and durable repair and replacement materials that avoid the need to repeatedly restore teeth. The focus of emerging applications of dental materials is primarily on the prevention,

detection, and treatment of caries, periodontal disease, and oral cancer. These materials are often called dental **biomaterials** because of the increase of interaction with the biological systems.

New dental biomaterials must satisfy the following requirements: (1) be nontoxic to human cells, (2) not support the growth of microbes and fungi, (3) be able to form an excellent seal between the oral cavity and underlying tooth structure, (4) be sufficiently **bioactive** to stimulate in vivo repair of tissues, (5) have properties similar to the tissue that is to be repaired or replaced, (6) exhibit handling properties that allow ease of manipulation and promote optimal clinical performance, (7) exhibit an esthetically pleasing appearance, and (8) are cost-effective.

In the following subsections, research and technologies are discussed for their relevance to solving oral health-related problems. **Figure 20-1** depicts a flowchart of basic, translational, and clinical research representing stages in the development of emerging technologies and products. The farther to the right of the chart

Research stage	Basic research	Applied/transitional research		Clinical trials		Applicability to dental practices	
Technology classification	Emerging technology concepts	Nanotechnology advances	Nanotechnology validation	Established nanotechnology	Integrated nanotechnology and microtechnology	Spin-off technology	Cost-benefit demonstrated
Testing stage	Hypothesis testing	Product evaluation	Bridge between basic/applied and clinical practice	Pilot and retrospective studies	Randomized controlled trials	Performance appraisal	Refinement of technologies
Outcomes	Preliminary data	Comparative performance	Preliminary evidence	Validation of evidence	Promising treatment outcomes	Optimum treatment outcomes	Adoption by clinical practices or dental labs
Stage of technology development	Technologies are feasible		Technologies are imminent or validated		Further refinement needed	Technologies applied to health care tasks	Oral health care goals fully achieved
Level of evidence	Clinical simulation	Proof of concept	Probability of specific outcomes	Limited applicability of technology	Application of refined technology	Demonstrated benefits in lab and clinic tasks	Fully documented and well-established evidence
Level of success	Desirable technologies, materials, and devices		Possible future technologies, materials, and devices		Probable future technologies, materials, and devices	Likely future technologies, materials, and devices	Proven future technologies, materials, and devices

• **Figure 20-1** Flow chart of basic, translational, and clinical research links to develop and evaluate emerging technologies and products. The downward arrows show the sequence of steps taken in the process. The rightward arrows show the increasing probability of having a desirable clinical outcome.

a technology or material is, the higher the probability that this material will have a desirable clinical outcome. The discussion is divided into three sections: biomaterials, biological materials, and instruments and processes.

Biomaterials

Any matter, surface, or construct that interacts with biological systems is considered to be a biomaterial. In the present context, only synthetically derived or highly processed nonsynthetic materials (materials of biological origin) are discussed. In dentistry, these are also preferably known as dental materials.

CRITICAL QUESTION

In which ways will nanotechnology provide products or processes that can improve oral health outcomes?

Nanotechnology

Nanotechnology uses nanosized particles and surface features with very high ratios of surface area to volume that are usually different in their bioactivity, solubility, and antimicrobial effects compared with larger particles of the same composition. Thus changes in properties cannot be extrapolated by an inverse linear analysis of particle size but must be determined through in vitro and in vivo testing of the nanomaterials. In dentistry, nanotechnology had been focused on the development of nanoparticle

fillers to improve dental composite esthetics. The use of nanotechnology today is more diverse.

In **biomimetics**, nanotechnology is being used to develop materials that promote hard tissue remineralization. Biomimetic materials and processes mimic those that occur in nature, particularly self-assembly of components to form, replace, or repair oral tissues. These concepts are discussed further later in this chapter.

For dental implants and related devices, nanoparticles are used to modify dental implant surfaces to influence the host response at the cellular and tissue levels. Electrophoretic sol-gel fabrication, pulsed laser deposition, sputter coating, and ion-beam-assisted deposition are among the approaches used to develop nanotextured, thin-film, biocompatible coatings for implant surfaces. These technologies reduce the thickness of the coating layer and increase the specific surface area and reactivity to improve the interaction with the surrounding apical tissue.

Important nanoparticles include metals, such as silver, and ceramic powders, such as silica and titanium dioxide. In situ-generated silver nanoparticles have been reported to be highly effective in restorative resins, bonding resins, and prosthetic resins for inhibiting a variety of biofilm-forming bacteria while not interfering with manipulation, curing, mechanical properties, or other performance properties. Silica nanoparticles already have wide use in dentistry, from toothpastes to composites. Titania nanoparticles are widely used for pigments in dental materials but lack the stronger antimicrobial effects of Ag.

Another recently introduced nanotechnology kills bacteria on contact on restoration surfaces. Infinix flowable composite

(Nobio Ltd., Israel), which contains quaternary ammonium bound to silica (also known as *QASi*) was reported to significantly reduce *Enterococcus faecalis* on the surface of the material without affecting composite flexural strength, radiopacity, depth of cure, water sorption, or water solubility. After 6 and 12 months of use in vivo, there was a 50% reduction of live bacteria on Nobio QASi composites compared with control composites. An added advantage of the QASi-containing surfaces is that no “recharging” is needed, unlike the fluoride in glass ionomers that confers microbial resistance. Prevention of bacterial biofilm protects the integrity of the dental product restorations.

Resin Restorative Materials

Despite the recent innovations in increasing the service life of contemporary resin composites (see “Innovations in Dental Composites” in [Chapter 5, Classification of Composites by Unique Properties](#)), significant uncertainty exists regarding the interactions of bacterial biofilms, wear, and fatigue leading to recurrent caries. Thus further improvements are needed in order to greatly increase the clinical life of resin-based restorations to match and even surpass the durability of amalgam, the gold standard, and eliminate the need to repair the restored teeth. To this end, major goals for restorative materials continue to be the reduction of composite shrinkage during curing, porosity, wear and attrition, improvement of the composite–dentin interface, and increasing the degree of conversion of resin monomers.

One factor that influences restorative longevity is operator error. Materials with many steps, the requirements for a dry field, difficult handling, or long curing times are inherently prone to mistakes that often lead to material defects, such as voids and inadequate curing, which hasten the onset of fatigue, fracture, and abrasion. Thus more technique insensitive (“forgiving”), operator-friendly, esthetic, and long-lived composites are being developed.

As discussed in [Chapter 5, Classification of Composites by Manipulation Characteristics](#), two novel flowable composites marketed as “bulk-fill, universal restorative resins,” G-aenial Universal Flo (GC America, Alsip, IL) and Surefil-SDR flow (DENTSPLY International, York, PA), among others, exemplify operator-friendly materials that are translucent and have flowable rheology, easy handling properties, and a large depth and degree of conversion. Both exhibit low shrinkage and shrinkage stress, which allow the composite to be placed in large increments instead of the prescribed 2-mm layers, further contributing to their technique insensitivity. Because these highly flowable composites contain reinforcing filler on a par with the highly loaded, nonflowable, and “packable” hybrids, such as those described in [Chapter 5, Classification of Composites by Manipulation Characteristics](#), their performance is similar to those of current posterior resins, raising expectations of high durability and long clinical life. Early-stage wear resistance and durability tests have validated the benefits of their high filler loading, low curing stress, and high level and depth of cure.

Filtek Universal (3M ESPE, St. Paul, MN) is a recent addition (2019) to the category of operator-friendly composites. The nanoparticle fillers in this composite provide superior shade matching and wear resistance. This composite contains two unique monomers: addition-fragmentation monomer (AFM) and aromatic urethane dimethacrylate (AUDMA). The AFM fragments and repolymerizes during curing, reducing curing stress and enhancing marginal integrity. The AUDMA decreases the number of reactive groups in the resin and increases polymer flexibility.

Fewer reactive groups moderate the volumetric shrinkage, and the increased polymer flexibility reduces the stiffness of the polymer matrix before the matrix reaches the gelation point. Both of these contribute to decreased curing stress, improved marginal integrity, and ultimately, improved abrasive wear resistance.

Omnichroma (Tokuyama Dental America) is a single-shade, universal composite that matches every tooth shade, from A1 to D4. The innovative material contains 260-nm spherical nanoparticles that can scatter red-to-yellow colors as ambient light impinges on and is reflected from the composite. The red-to-yellow scattering blends with the scattered light of the adjacent dentition to produce an esthetic color match and reduces operator sensitivity.

Bioactive Materials

Most present-day dental materials do not induce dental tissue responses and are not bioactive. *Bioactivity* is defined in ISO 23317 as a property that elicits a specific biological response at the interface of the material, which results in the formation of a bond between tissue and material. As such, bioactivity incorporates antimicrobial, remineralizing, and bone-forming materials, as discussed in this section. Bioactive materials implanted in a living body form a thin layer rich in Ca and P on their surface. The material then connects to the living tissue through this apatite layer without a distinct boundary. Bioactive materials are useful for the healing of tissues, especially pulp and periapical tissues, and for supporting root development in immature teeth.

Bioactive materials available now include calcium hydroxide, bone grafts, bioglass particulates, and hydraulic (water-setting) ceramic powders. The calcium–silicate powders are considered the gold standard for endodontic surgical procedures, pulpotomy, revascularization, and apexification procedures. The calcium aluminate-based powders, being more acid-resistant, are being used with glass ionomers for supragingival cement for prosthodontics and have found limited use for restorative applications. Their acid resistance makes them useful for infected sites, which are generally acidic; as such, the aluminates may be used for the same indications as mineral trioxide aggregate (MTA) materials. Calcium phosphate cements are generally slower-setting than the hydraulic cements but are being used for scaffolding purposes where the formation of hydroxyapatite is necessary and porosity is acceptable.

Theobromine, a xanthine found in cocoa, promotes the formation of hydroxyapatite mineral and increases the size of hydroxyapatite crystals by upregulating osteogenesis, which would have numerous benefits. For instance, theobromine may remineralize adjacent tooth enamel and have the potential to close gaps between restoration and tooth, improve bond-strength durability associated with reduced bond degradation, and enhance bone integration with implant surfaces. The large crystallite size leads to resistance to dissolution via the decreased specific surface area available for acid dissolution. New bioactive materials are under development that, in general, will create a biomimetic “presence” in vivo that induces healing superior to those of many present-day dental materials.

Dental resins have been combined with bioactive TiO₂ nanoparticles to promote hydroxyapatite formation, enhance mechanical strength, and act photo-catalytically as a bactericidal agent. A dentin bonding adhesive with TiO₂ nanoparticles can provide on-demand, photo-induced microbial inhibition and simultaneously fill marginal gaps via remineralization of adjacent dentin and enamel. This technology may reduce recurrent caries, improve tissue integration with implant surfaces, and prevent peri-implantitis or other infections at

the tissue–implant interface. These results are intriguing and highly promising, but they have not yet been tested clinically.

The surface of materials is often what makes them bioactive. Titanium as an implant material is an example. Like chromium, titanium spontaneously reacts with oxygen to form a self-repairing, protective oxide layer (TiO_2), which makes the implant surface largely corrosion-resistant, inert, and biocompatible. However, surface roughness and other aspects of surface topography, together with surface chemistry, are also known to strongly influence the early events in healing and osseointegration that follow implant placement. Interactions between proteins, cells, tissues, and implant surfaces play a role in determining the success or failure of all implanted materials and devices. The surface chemistry and topography-related mechanisms that control these events are poorly understood. Nevertheless, substantial research effort in dental implantology is currently directed at developing surfaces with controlled topography and chemistry at the nanoscale level to optimally promote protein adsorption and cell adhesion. Biomimetic calcium phosphate coatings for implants are under development to enhance **osteoconductive** properties and incorporate biological agents to accelerate bone healing in the peri-implant area. Overall, these research efforts to understand and control surfaces are showing great promise, and some are likely to lead to materials, processes, and/or procedures to enhance the reliability of placement, indications for use, and the success rate of dental implants.

Antimicrobial Materials

Preventing and removing biofilms is important for pediatric dentistry and especially periodontics and endodontics. Adjunctive liquids are needed that can quickly kill and remove bacterial colonies in biofilms during periodontal scaling. In endodontics, new irrigants are needed to better remove and deactivate smear layers containing remnant bacteria after root canal preparation, which is never complete. Some endodontic irrigation liquids are combined with acids or surfactant to dissolve the dentinal smear layer created by endodontic instruments in a root canal. Combination devices containing a drug, bone morphogenetic protein (BMP), or amino acids are envisioned for endodontic and periodontal uses. Two such combinations, QMIX and MTAD (DENTSPLY Inc.), are irrigants in endodontics.

Endodontics has been dramatically changed by the introduction of hydraulic ceramic (water-setting) cements that create high-pH environments and thereby have antimicrobial properties. For example, the tricalcium silicates and calcium aluminates have enhanced endodontic and pulpal treatment with their antimicrobial properties and dimensional stability.

Although the clinical performance of dental resins has improved remarkably in durability, bond strength, and esthetics, most still lack antimicrobial properties and allow bacterial colonization and biofilm formation. Antimicrobial monomers are being investigated and developed to prevent recurrent caries better than composites that release fluoride ions. Ideally, the polymerized resins would have sustained antimicrobial characteristics. Examples include modified (chlorinated) polyethylene or other polymers that may provide antimicrobial activity.

CRITICAL QUESTION

What stages of research will lead to the adoption of new remineralizing materials and processes for dental practice?

Remineralizing Agents and Materials

The dental literature reflects a strong demand for preventive and “healing” therapies for individuals at moderate risk for caries to prevent a shift to a high level of risk. Thus low concentrations of fluoride are included in toothpaste, well water, and other fluoridated sources to have beneficial effects on enamel and dentin remineralization.

Other remineralizing agents include the use of nanoparticles of hydroxyapatite because they are on the same crystalline scale as naturally occurring hydroxyapatite crystals in enamel or dentin. A promising example of this approach was reported by Li et al. in 2008, who found that 20-nm nanohydroxyapatite particles had a superior anticaries repair effect compared with that of larger hydroxyapatite particles.

Liquid remineralizing dentin bonding agents, which should wet, flow, and completely fill the demineralized zone created by etching prior to or simultaneous with bonding to the restorative material, are also being developed. For instance, a tricalcium silicate product was tested with polyacrylic acid and sodium tripolyphosphate for remineralization. When these materials were applied under a restorative material, the combined material infiltrated the demineralized collagen fibrils with precursors that restored the calcium phosphate at the interfaces of the dentin and the restorative material. Incorporation of some of these technologies into primers and dentin bonding agents are expected to both inhibit caries activity and increase the service life of composite restorations.

Theobromine, a bioactive agent discussed earlier, is an alternative to fluoride as a remineralization agent. Theobromine is currently used in Theodent toothpaste products (Theodent LLC, New Orleans).

Emerging technologies and materials that promote remineralization at early and moderately advanced stages of caries are being developed more rapidly now that highly sensitive imaging and measurement processes are available ([Chapter 15, Diagnostic Systems](#)).

Bone-Grafting Materials

In addition to remineralizing small lesions, gross remineralizing treatments and bone grafts are increasingly needed for dentistry. Bone-grafting materials are necessary for various oral surgeries, such as alveolar ridge augmentation and sinus augmentation, and for the placement of implants or to improve mandibular denture stability. Extraction socket grafting materials are gaining popularity to prevent the collapse of cortical bone and enable the placement of an implant. Also, patients prefer faster treatment and fewer surgeries, which drives research and development toward single-stage implant procedures with immediate functional loading (IFL). Implants with nanotechnology coatings may increase the success and acceptability of the single-stage and IFL procedures, but before implant placement, grafts are often needed.

Graft materials are available containing allogeneic, xenogeneic, or synthetic hydroxyapatite particles to act as a scaffold for gradual replacement by the patient's bone. These current bone grafts slowly resorb, and the replacement bone densifies over months until a restorative denture or implant can be made. More rapid resorption and bone-growth-stimulating materials are needed to meet the demand for faster implant placement after tooth extraction, even immediate placement. Some available grafting materials are designed for faster resorption and bone growth. For instance, PepGen P-15 (DENTSPLY Friadent, Mannheim, Germany), a

hydroxyapatite product with an amino acid, is available for accelerating natural bone regeneration. Infuse (Medtronic, Minneapolis, MN), a collagen sponge with recombinant human bone morphogenetic protein-2 (rhBMP-2), is indicated for sinus augmentation and localized alveolar ridge augmentation. BMPs, also known as *cytokines*, represent a group of growth factors that can affect cell interactions and cell behavior. PerioGlas and NovaBone Dental Putty (NovaBone Products, Jacksonville, FL) contain coarse ($>100\text{ }\mu\text{m}$) bioglass particles for implantation as a resorbable scaffold for bone growth and periodontal grafting. Ostim-Paste (aap Biomaterials GmbH, Dieburg, Germany) is a nanocrystalline hydroxyapatite paste that can be used to repair the intraoral bony defects that may result from cystectomies (a surgical procedure to remove a cyst), root tip resections, extractions, and surgical tooth removal; for augmentations in the areas of the alveolar processes and maxillary sinuses (sinus lift); and for filling periodontal defects. Clinical trials are needed to determine the success of each of these approaches and guide the development of future products.

New bioactive glasses are under development that contain more boron and silica than the original formulas of 45S5 bioglass (45 wt% SiO_2 and a 5:1 ratio of CaO to P_2O_5) for *osteogenesis*, and the new formulas may be resorbed more quickly, with faster bone replacement. Copper or silver in these glasses may also enhance soft tissue deposition in other applications. Powders, fibers, or foams of the bioactive glasses may be used as scaffolds for use in the rapid replacement of bone or soft tissue. Scaffolds of bioactive glass are used for osteoconduction, and they may also initiate the development of cartilage (*chondrogenesis*). The latter could be useful for temporomandibular joint (TMJ) treatments. Combinations of biodegradable polymers with bioactive glass particles may also enhance tissue replacement and serve as the basis for new grafting materials.

CRITICAL QUESTION

In which ways does the use of smart materials lead to improvements in the quality of oral health care?

Stimulus-Responsive “Smart” Materials

“Smart” materials are designed for interaction with external stimuli, such as light, temperature change, stress, moisture, pH, or electric/magnetic fields. Examples of such dental materials include zirconia ceramics that transform from a tetragonal to monoclinic crystal form when tensile stress is induced at crack tips, leading to an increase in crystal volume and compressive stress to prevent the propagation of cracks. Light-curing composites begin curing when irradiated with particular wavelengths of blue light, and others change color when irradiated (for use in orthodontics). Glass-ionomer cements will weaken when desiccated, making orthodontic bands easier to remove. Other glass-ionomer restoratives increase the release of fluoride when the pH in plaque fluid decreases (becomes acidic). Nickel-titanium wires are designed to soften when chilled below body temperature for bending and threading through orthodontic brackets. Smart cements have been envisioned to soften and allow debonding by a temperature change or irradiation process for the removal of orthodontic devices, indirect restoratives, and some implant components.

Secondary caries and the unnecessary replacement of defective restorations can be prevented and adjacent enamel remineralized through one of the following preservative treatments: (1) sealing of marginal crevices adjacent to defective restorations with

a hydrophilic resin, (2) sealing crevices with a smart resin capable of the controlled release of chlorhexidine or another antibacterial agent, (3) sealing crevices with a smart resin capable of the controlled release of fluoride, and (4) applying a sealing resin or varnish that can release xylitol or other caries-management agents at specified concentrations over a specific period of time. Emerging technologies and materials for sealing may include smart hydrophilic resins that release fluoride and/or other mineralizing agents when the pH of oral fluids decreases to a range of 4.0 to 5.5 to seal moist microscopic crevices adjacent to defective restorations and reduce enamel demineralization. Improved, smarter sealants, varnishes, and composites that release fluoride would be beneficial. Concomitant studies of composition, particle size, and particle-size distribution for smarter release of fluoride (on-demand release) would make them “smart sealants.” The rapid induction or reversal of anesthesia may be another future application for smart materials. For instance, particles or substances applied in the sulcus could start or stop the anesthetic reaction. Smart material concepts can provide the clinician with better control, which will certainly suggest approaches for new products.

Self-Assembling Materials

Self-assembling materials automatically construct prespecified assemblies. Viruses, cells, tissues, and whole organisms are examples of biological self-assemblies, whereas crystals are an example of nonbiological self-assemblies. The latter can be derived from polymers, metals, ceramics, or combinations of components. Self-assembly occurs by orchestrated stages of initiation, propagation, and termination. Control systems for initiation and/or propagation may be templates (e.g., template polymerization of proteins, patterning of silica templates for electrical circuits), or they might depend simply on natural rules corresponding to energetically favorable physical, chemical, mechanical, and/or biological events (e.g., capillary forces, heterogeneous nucleation of crystallization, surface-energy reduction, phase separation, micelle formation, and steric probabilities for molecular folding).

Bone or soft tissue scaffolding of graft materials can be considered as self-assembling. The coarse porous particulate or spongy bone graft materials are designed to encourage biological tissue to respond and replace the scaffold. Templates of proteins may be used to encourage biological events, such as specific tissue growth. For example, a broad class of self-assembling peptide derivatives offers exciting novel therapies of broad potential impact in regenerative medicine. These peptide amphiphiles (PAs) incorporate a short hydrophobic domain on one end of a hydrophilic oligopeptide sequence that also contains bioactive signaling sequences. Nanostructures can be designed from these peptides through self-assembly strategies and supramolecular chemistry, having the potential to combine biocompatibility with bioactivity. Such structures offer engineering design flexibility for biomedical and biomaterials applications. This type of research is nearing clinical application. However, for the regeneration of teeth, translation remains a distant but achievable target. Possibilities involve tissue engineering, biomimetics, and stem cell biology, which are discussed in greater detail in the following sections.

Self-Healing (Self-Repairing) Materials

Self-healing is an *autonomically* initiated response to damage or failure. Nature continually remodels bone, which can heal itself (self-repair) even after a major fracture. Nature’s mechanisms of

repair have inspired efforts to develop self-healing capabilities in synthetic materials that may well appear in dental products within a few years. To achieve self-healing, a material must be capable of identifying and repairing failures.

Restorative materials are subject to aging *in vivo* and have a limited lifetime; they gradually degrade because of physical, chemical, and biological phenomena such as creep, fatigue, internal stresses, dissolution, erosion, or biodegradation. An epoxy system has been developed that is self-healing, consisting of microencapsulated dicyclopentadiene and Grubb's metathesis catalyst. If a crack occurs in the epoxy composite, some of the microcapsules are ruptured near the crack and release dicyclopentadiene, which subsequently fills the crack and reacts with the catalyst, causing polymerization of the dicyclopentadiene and repairing the crack. These materials improve the recovery of composite fracture toughness after stress in laboratory tests. Similar systems have exhibited a significantly longer service life under mechanical stress *in situ* compared with those without the ability for self-repair. A self-healing dental resin would be extremely important for lengthening service life.

Biological Materials

Biomaterials science is exploring new technologies and is increasingly shifting to natural tissue repair or replacement therapies. Biological biomaterials can lead to natural tissue restoration but rely heavily on tissue engineering, biomimetics, self-assembling systems, cell biology, and regenerative dentistry.

Biomimetics

Some biological mechanisms and processes (e.g., protein synthesis, silk and seashell formation) can be mimicked by synthesizing similar products by artificial mechanisms. Of particular interest here are those that involve self-assembly of components to form, replace, or repair oral tissues. An intriguing prospect for this approach is the use of self-assembling PAs that contain both a photopolymerizable group and the arginine-glycine-aspartic acid-serine (RGDS) cell-adhesion sequence. The self-assembling nature of the PAs causes the formation of networks of prealigned nanofibers, mimicking natural fibers. These nanofibers can be formed into tissue scaffolds as substrates for mesenchymal stem cell (MSC) cultures. Topographical patterns produced from aligned PA nanofibers were found to promote the alignment of MSCs, which indicated that the cells sensed and responded to the nanoscale features of the scaffold surfaces. The aligned MSCs then differentiated to form bone-like tissue.

Biomimetic technologies are under intense investigation for translation into clinically useful materials and treatments. These and other biomimetic approaches and the use of tissue engineering scaffolds are discussed further in the sections headed "Tissue Engineering" and "Regenerative Dentistry."

Tissue Engineering

Tissue engineering has emerged in the past 30 years as a multidisciplinary field recognized by the National Institutes of Health involving biology, medicine, and engineering. Experts hope that tissue engineering will revolutionize health care and improve quality of life for people worldwide by maintaining, restoring, and enhancing tissue and organ repair, regeneration, and function. The main requirements for engineered tissues are the appropriate

levels and sequencing of regulatory signals, the presence of responsive progenitor cells, an appropriate extracellular matrix or carrier construct (i.e., scaffold), and an adequate blood supply for oxygen and nutrients. Either biological or synthetic polymers are used to form the tissue engineering scaffolds. Recent advances in understanding growth factors and biodegradable polymer scaffolds have made possible the successful tissue engineering of cartilage, bone, and related tissues. Nakashiwa and Reddi (2003) have summarized the remaining achievements required to develop the clinical techniques needed for the creation, substitution, and/or replacement of dental tissues. Among the many potential applications are fracture repair, dentin and periodontal ligament replacement, alveolar ridge augmentation, temporomandibular joint reconstruction, preosseointegration of dental implants, pulp regeneration, and partial or whole tooth regeneration.

Tooth loss is the most common organ failure. The regeneration of a tooth can include not only regrowth of the entire tooth complex as a complete biological organ but also the regeneration of individual components, including enamel, dentin, pulp, cementum, and periodontal tissues. Two lines of investigation deal with restoration of partial tooth damage using tooth-related stem cells for the repair or whole-tooth regeneration by using stem cells or tissue-engineering techniques. The first successful bioengineering of entire tooth structures was reported in 2002 using cells from dissociated porcine third molar tooth buds seeded on biodegradable polymer scaffolds that were implanted in rat hosts for 20 to 30 weeks.

Osteonecrosis is a new and serious dental disease that arises from receiving bisphosphonates intravenously or orally to treat other medical conditions. Conventional debridement is ineffective in treating osteonecrosis, so biological solutions are being developed to treat the condition and to prevent the onset of other dental events, such as surgeries or extractions.

Chronic periodontitis is one of the most common oral diseases worldwide, after caries. In periodontics, tissue-engineering strategies are being developed to serve as periodontal regenerative therapies for the restoration of lost alveolar bone, periodontal ligament, and root cementum. These strategies are based on the growth of new functional tissue rather than replacement of the periodontium. These studies have shown that regeneration is feasible for small to moderate-sized periodontal defects using cell-scaffold constructs for future clinical use. Yet even though tissue engineering has created the means for predictable and optimal periodontal tissue regeneration, routine clinical periodontal regenerative medicine and clinical use remain in an early stage.

Still greater challenges are major bone reconstruction after trauma or cancer and augmentation following implants. Formidable challenges exist for regenerating normal bone structure and restoring the functionality of tooth-supporting tissues. Possibilities depend on an understanding of the cellular and molecular mechanisms involved in periodontal tissue regeneration, the differentiation potential of stem cells, and the interactions among stem cells, scaffolds, and host tissues. Intense research and development activities in these areas indicate that placing implants may soon be possible, even under adverse anatomical or biological circumstances. Tissue engineering may soon lead to the reconstruction of lost bone in bone deformities more effectively and less traumatically than the traditional autogenous bone-transplantation approach.

Predicting the full impact of tissue engineering on the future of dentistry is difficult. However, tissue engineering brings together advances in disparate areas of materials science, genetics,

molecular biology, and cell biology. Researchers in these disciplines may develop new alternatives for the regeneration of soft tissues, bone, and enamel. An important consideration will be the cost of these procedures, at least initially. Not only is the cost of treatment important, but the costs are significant for such projects to develop the technology, demonstrate clinical efficacy, meet regulatory requirements, commercialize the technology, and train clinicians in these innovative techniques.

Delivery Systems for Biologicals

Tissue-engineering approaches that combine biomaterials with biological materials, such as proteins (growth factors, etc.), genes, and cells (both differentiated and stem cells), are promising routes to the therapies discussed previously. Thus biological materials are a source of active, ongoing research directed in part toward developing competent scaffolding materials capable of fulfilling application-specific requirements for biodegradation, biocompatibility, mechanical stability, biofunctionality, and processability. The key attributes of any biological delivery system are controlled, sustained, and targeted release of drugs and bioactive factors. Each of these attributes is fundamentally dependent on the ability to predictably generate a functionalized material.

An example of a promising biological delivery strategy is to increase osseointegration of titanium implants by coating them to improve healing, induce peri-implant bone formation, and enhance osteointegration. Coatings may include extracellular matrix components, such as collagen, BMPs, or other proteins. Further developments are required to orchestrate the release pattern, optimize the time that the active components remain bioactive, control degradation, optimize the extracellular matrix that forms on the implant surfaces, and achieve maximum bone formation at minimal concentrations of the biological material.

A regenerative approach for diseased or necrotic pulp tissue includes tissue removal and replacement with healthy tissue, including melanocortin peptides (melanocyte-stimulating hormone, α -MSH), which possess antiinflammatory properties. A nanostructured and functionalized multilayered film containing α -MSH was reported for endodontic regeneration. Applied as a gel or strip, MSH films were placed adjacent to the damaged tooth to encourage the growth and regeneration of cells. In tests performed on cavity-filled mice teeth, researchers saw extremely positive results; after a month, the cavities had disappeared. This technology is in its formative stages.

Many approaches may be viable for biological materials in dentistry, but several more years will be required before a version is available for general use in dental practice.

CRITICAL QUESTION

Why are engineered tooth roots more likely to have a greater impact on dentistry than the engineered whole teeth now under development?

Regenerative Dentistry

Restorative dentistry is gradually transitioning toward biologically driven repair, replacement, and regenerative medicine therapies and away from replacement therapies using synthetic materials. For tooth regeneration, the two major approaches are scaffolds seeded with stem cells and stem cells without scaffolds. For these approaches, the mouth has special advantages compared with

other body locations, such as minimally invasive access and ease of observation within the oral cavity.

Five dental stem cells have been isolated: (1) dental pulp stem cells, (2) stem cells from exfoliated deciduous teeth (SHEDs), (3) stem cells from apical papillae (SCAPs), (4) periodontal ligament stem cells (PDLSCs), and (5) dental follicle progenitor cells. These cells can differentiate into odontoblasts, adipocytes, neuron-like cells, glial cells, osteoblasts, chondrocytes, melanocytes, myotubes, and endothelial cells. Thus they will eventually be used to grow replacement human teeth, but the signaling processes that control the development of discrete dental morphologies for incisors, canines, premolars, and molars must be better understood before whole-tooth regeneration will become a practical goal.

Instead, the repair and regeneration of dental tissues such as dentin, pulp, periodontal ligaments, and whole root structures offer possibilities for earlier realization than whole-tooth regeneration. The treatment tends toward either a cell-based or cell-attraction mechanism. One example of this strategy is regenerative endodontic treatment of infected, immature, permanent teeth by Meschi and Lambrechts, who disinfected the root canal and introduced stem cells, growth factors, and scaffolds. Another strategy using pulp tissue engineering and transplantation has been applied in vitro to promote tissue regeneration. The cell-attraction concept has been applied both in vitro and clinically and resulted in recovery rather than regeneration of the pulp–dentin complex. Long-term results are still lacking, and thus there is a need for further clinical, microbial, and translational research.

Another step was taken toward regenerative endodontics when pulp tissue was generated from the cells of human exfoliated deciduous teeth blended with nanofiber peptides as a scaffold material and injected into root canals. A similar approach using the self-assembling PAs, discussed previously, as scaffolds to encapsulate stem cells from deciduous teeth revealed that they proliferate and secrete a soft collagen matrix. At this time, many challenges remain; however, it is foreseeable that stem-cell/tissue-engineering therapies will become available in the near term to stimulate the pulp to deposit dentin and continue natural root growth in noninfected, accidentally injured immature teeth.

Regeneration of the tooth root represents another feasible near-term goal. This was demonstrated by transplanting a root-shaped calcium phosphate block loaded with swine SCAPs coated with a resorbable gelatin containing PDLSCs. When this block was placed into the extraction socket of a minipig lower incisor, a root/periodontal structure was generated that was sufficient to attach a ceramic crown. SCAPs are easily accessible because they can be isolated from human third molars. The development of a combination of SCAPs and PDLSCs encapsulated in a resorbable scaffold offers a relatively near-term means of clinically inducing the regeneration of a root form and connective tissue in alveolar bone for the attachment of an artificial crown.

Both biomaterials and biological materials are playing an indispensable role in the progress toward regeneration of a tooth root, a crown, pulp, dentin, enamel, or an entire tooth. Repair occurs by the use of metals, ceramics, or synthetic resin materials, whereas regeneration is controlled by biological processes. Tooth regeneration is an extension of concepts in the broad field of regenerative medicine to restore a tissue to its original form and function by biological mechanisms. Although substantial progress has been and is being made, whole-tooth regeneration remains a distant but achievable goal—one that would cause dentistry to undergo a paradigm shift from repair and replacement to regeneration.

CRITICAL QUESTION

In what ways do emerging diagnostic tests and processes improve the quality of dental treatment?

Instruments and Processes

Diagnostic Devices and Techniques

As discussed in [Chapter 15, Diagnostic Systems](#), various new and evolving modern diagnostic techniques have been introduced for caries, periodontal disease, oral cancer, herpes simplex infection, and candidiasis, as well as for incipient fractures and trauma. Promising technologies may produce images directly from the patient or use saliva or other biological specimens from the patient being treated. Diagnostic instruments have been based on radiographic, optical, laser fluorescence, ultrasound imaging, and electrical conductance technologies. A selected group of those that appear to be the more promising in the near term are discussed in the following sections.

Cone-Beam Computed Tomography

In dentistry, cone-beam computed tomography (CBCT) provides high-resolution, low-distortion, 3-D digital imaging of the hard tissues of the head. Thus instead of pixels, the resolution is measured in **voxels**, and the images are often sharper than conventional CT images. The term *cone-beam* refers to the cone shape of the x-ray beam used to create multiple thin slices instead of the fan-shaped beam in conventional CT. CBCT produces Panorax and cephalometric projections, which become 3-D images when the data are reformatted in a volume. The images that result can be manipulated with the instrument's visualization software from any point of view (e.g., in the axial, coronal, sagittal, and cross-sectional planes). Layers can be "peeled away" to show hidden underlying anatomical structures and defects. The slice thickness can be changed, and the structures can be tilted, zoomed, and highlighted. These new views can drastically change treatment decisions.

Swept-Source Optical Coherence Tomography

Swept-source optical coherence tomography (SS-OCT) is a CBCT-related technology that uses infrared laser optics rather than x-rays to generate high-resolution cross-sectional images of microstructures in biological systems. This technology has been under development for many years for various medical imaging tasks, including examination of the oral cavity. Recent progress indicates that a practical device may be available for dental applications within a few years. This nonionizing, real-time tomographic technology can detect structural flaws at a submicron scale for dental diagnostic tasks. For example, SS-OCT may be used to monitor the accuracy of composite restoration placement, the development of polymerization contraction gaps, the detection of vascular lesions, and the detection of occlusal caries.

Laser-Induced Fluorescence

Quantitative light-induced fluorescence (QLF; Inspektor Research Systems, Amsterdam, Netherlands) is a well-advanced technology, although it is not widely used in routine dental practice. QLF is a simple yet effective technique that detects and quantifies de- and remineralization of dental tissue and bacterial activity to reveal lesions in teeth before they become frank lesions or cavities. The

QLF method is based on the autofluorescence of teeth and plaque microorganisms. When teeth are illuminated with high-intensity blue light, they fluoresce (re-emit) light in the green part of the spectrum; less light correlates with less mineral content in the enamel. Also, bacterial metabolic activity and plaque formation can be detected because they produce porphyrin-type biological pigments that fluoresce red light. This technique provides a measure of the degree of existing enamel demineralization via a small video sensor. A digital image of each tooth is collected, which can be analyzed for the amount of enamel loss. White spot lesions (early dental caries) can be detected and quantified, as can bacterial metabolic activity on and in the teeth. When lesions are identified at an early stage, the teeth can repair themselves if good oral hygiene practices are followed. This method also allows either the dentist or oral hygienist to provide the patient with immediate information and a direct incentive to monitor the quality of oral care procedures. The newer QLF-D BiLuminator collects white light and fluorescence images simultaneously to allow assessment of leaking restoration margins, secondary caries, occlusal and interproximal caries, sealant integrity and cariogenic activity under sealants, calculus, and gingivitis.

Laser Photothermal Radiometry

Laser photothermal radiometry (PTR) detects a small temperature rise modulated by thermal infrared (black-body) radiation emitted from hard dental tissue after absorption of the laser light and its nonradiative energy. In translucent materials such as enamel and dentin, depth information is obtained following optical-to-thermal energy conversion and transport of the incident laser power in two modes: (1) the heat conductivity from a near-surface distance (50 to 500 μm), controlled by the thermal diffusivity of enamel and radiatively through black-body emissions from several-millimeter depths, owing to optical penetration of the diffusely scattered laser-induced optical field; and (2) partial infrared transparency (infrared "spectral windows") of the hard dental tissue, which allows the thermal photons to exit the enamel and register on the detector.

Two variations on this emerging nondestructive technology for exploiting the opto-thermo-physical properties of teeth have been reported. Both take advantage of the effects that changes in porosity and the crystalline status of enamel have on the thermal and optical properties of hard tissues. As cariogenic demineralization and formation of subsurface lesions grow, optical scattering and absorption increase, whereas thermal conductivity and diffusivity decrease. The two detection modalities are called *infrared photothermal radiometry and modulated luminescence* (PTR-LUM) and *thermo-photon lock-in imaging* (TPLI).

PTR-LUM (The Canary System, Quantum Dental Technologies, Inc., Toronto, Canada) scans a tooth with a low-power pulsating (modulated) laser light. The light is scattered, absorbed by the tooth, and then re-emitted at a longer wavelength as luminescence, and heat is generated ($<1^\circ\text{C}$). Simultaneously, heat (mid-infrared) and light (near-infrared) are measured to provide information on the presence and extent of decay up to a depth of a few millimeters below the surface.

TPLI uses a laser beam to illuminate the whole tooth and a midinfrared camera in the lock-in mode to produce images at a fixed frequency. TPLI is an extension of PTR into a full imaging modality. TPLI uses the same physical photothermal wave principles as PTR: increased light scattering and absorption by a carious lesion increase the thermal-wave amplitude and shift the thermal-wave centroid closer to the surface, producing contrast

between a carious lesion and intact enamel in both amplitude and phase images. TPLI phase images are emissivity-normalized (just as PTR phases are) and therefore are insensitive to the presence of surface stains. Amplitude images provide integrated information from deeper enamel regions because of the radiative contributions that overlap conductive heat transfer. TPLI imaging is noncontacting and is reported to have a higher sensitivity to very early demineralization than do dental radiographs.

Ultrasound Imaging

Better termed *ultrasonography*, this well-established medical diagnostic imaging technique has recently shown promise for high-resolution imaging with enhanced specificity and sensitivity for the early detection and monitoring of several oral pathologies. Ultrasonography is nonionizing and noninvasive, and with further development, handheld devices could become available for the detection of cracks, calculi, and periapical lesions, in addition to enamel and dentin demineralization caused by caries under and around existing restorations or on occlusal and interproximal surfaces.

Infrared Spectroscopy for Multiple Inflammatory Parameters

An optical spectroscopy instrument is under development to enhance the early detection and monitoring of peri-implant inflammation and thereby reduce the number of implant failures. The instrument uses visible, near-infrared spectroscopy to measure alterations in regional tissue hemodynamics in periodontal tissue. Tissue oxygenation at peri-implantitis sites is substantially reduced compared with healthy sites because of increases in deoxyhemoglobin and decreases in oxyhemoglobin at the peri-implantitis sites. To diagnose these changes, the instrument simultaneously measures tissue oxygenation, total tissue hemoglobin, deoxyhemoglobin, oxygenated hemoglobin, and tissue edema.

Salivary Genetic Testing

Genetic testing using saliva is a molecular biology–based analytical test particularly apropos for periodontal disease and oral cancer. Chairside salivary sampling can be analyzed by companies such as OralDNA Labs (Brentwood, TN) to identify patients who are genetically susceptible to periodontal disease. This genetic testing for the interleukin-1 (IL-1) gene cluster, a significant inflammatory mediator, complements other periodontal screening procedures and salivary bacterial DNA tests for specific oral pathogens. Saliva analysis is used to screen for oral human papillomavirus (HPV), especially the variants HPV-16 and HPV-18, as potential etiological agents in the development of squamous-cell carcinoma of the head and neck. Diagnostic testing will continue to expand and enhance treatment modalities. Such tests can enhance patients' acceptance of treatment plans and improve their cooperation with the clinician to improve periodontal health.

Liquid-Based Cytology

Liquid-based **cytology** is a relatively new screening technique approved by the U.S. Food and Drug Administration (FDA) for oral infections. It relies on the minimally invasive collection of transepithelial mucosal cells and other microbiological aspects for processing and evaluation. A clinician can request tests for several generalized oral conditions, such as herpes simplex infection and candidiasis, or suspicious areas of leukoplakia or erythroplakia (OralCDx, CDx Laboratories, Suffern, NY). Cytology provides the evidence needed to determine whether an immediate invasive full-thickness biopsy procedure should be performed.

Diagnostic technologies, such as CBCT, quantitative laser fluorescence (QLF), and salivary genetic testing, are at hand and growing. These and other techniques are expected to increase, with positive benefits for both clinicians and patients. Each technique varies with the mode of action and in its capability as a diagnostic aid. Differences in presentation and behavior among anatomical sites make it unlikely that any one diagnostic modality will have adequate sensitivity and specificity for all circumstances. Thus a combination of diagnostic tools will continue to be needed to reliably diagnose oral diseases and conditions and to provide corrective or preventive treatment at a stage where these treatments can be most effective.

CRITICAL QUESTION

How does computer-aided design/computer-aided manufacturing (CAD-CAM) production of dental prostheses differ from the processes of stereolithography, robocasting, powder-bed ink-jet printing, and laser scanning?

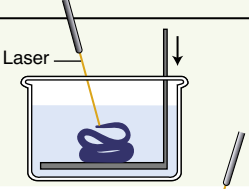
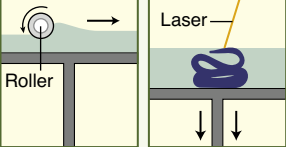
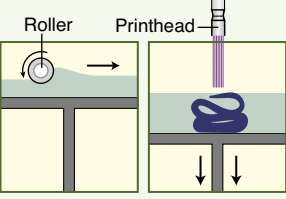
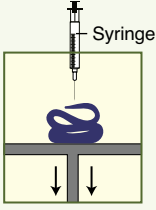
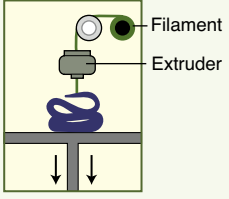
Computer-Driven Fabrication Systems

The present dental **CAD-CAM** systems vary dramatically in their capabilities. Both copy milling and true CAD-CAM systems have been developed. No equipment can acquire data directly in the mouth, but intraoral sensors are used to acquire data. Not every type of restoration can be created by CAD-CAM, although indications continue to expand. Both “additive” and “subtractive” systems are available. Temporary crowns can be made in the lab using either CAD or CAM systems. The additive systems use the programmed buildup of a design from a resin that is cured “voxel by voxel” to create the device. This requires resins that are cured in special computer-controlled lab equipment with ultraviolet light. Three-dimensional printing techniques have been developed for the formation of ceramic or resin composite restoratives (see [Chapter 15, Prototyping Tools](#)). Three-dimensional printing techniques will continue to grow and use enhanced dental materials, especially for fixed prosthodontics. The 3-D printing techniques are beginning to be used to fabricate the metal framework of dental crowns and bridges. More advanced dental applications include the creation of bone-graft scaffolds. Those developed to date are summarized in [Figure 20-2](#). See [Chapter 15](#) for a full discussion of these technologies.

Ceramic crowns, metal crowns, and metal superstructures (overdenture bars) have been made using the subtractive (machining) CAD-CAM method using blocks of zirconia, leucite-containing porcelain, filled resins, cobalt-chromium alloy, and titanium. Refinements and esthetic improvements are expected for all of the present systems.

Another emerging area is 3-D bioprinting. In 2019, [Grigoryan et al.](#) demonstrated the creation of blood-vessel networks and organ-like topologies using biocompatible hydrogels with tartrazine, a yellow food color additive projection stereolithography. The technique involves polymerizing material using blue light, one thin layer at a time. To make the technique work, the light must be confined to a single layer so that it does not penetrate to previous layers and polymerize them in off-target geometries. Tartrazine absorbs blue light selectively so that intertwined vascular networks rapidly form in highly defined geometries.

These emerging technologies will dramatically expand the capabilities for 3-D printing, but they will also require a different set of dental and laboratory technical training skills.

TECHNIQUE	SMALLEST PRINTABLE FEATURE	MATERIALS
Stereolithography Laser cures photopolymer as platform lowers into liquid vat. 	1–70 μm	Photopolymers
Laser sintering Laser melts powder rolled onto platform. Platform lowers with each layer printed. 	45–100 μm	Metals Polymers
Powder-bed ink-jet printing Printhead sprays liquid binder onto powder to fuse layers. Platform lowers with each layer printed. 	350–500 μm	Ceramics Metals Polymers
Robocasting Syringes extrude fluid materials that harden on lowering platform. 	200–400 μm	Biopolymers Some metals Food
Fused deposition modeling Heated extruder melts plastic filament, which cools on lowering platform. 	260–700 μm	Thermoplastics

• **Figure 20-2** The technologies available for three-dimensional printing. A variety of techniques can use various materials to build solid objects with different resolutions. The arrows indicate the direction of roller and platform movement. (Adapted from Butscher A, Böhner M, Hofmann S, et al: Structural and material approaches to bone tissue engineering in powder-based three-dimensional printing, *Acta Biomater* 7:907–920, 2011.)

Summary

This chapter has focused on technologies that are in the early stages of implementation and those that have not yet passed the proof-of-concept stage shown in the “level of evidence” section of [Figure 20-1](#). Technologies that promote 3-D remineralization are needed by practicing dentists whose focus is on disease prevention, minimally invasive procedures, and improved methods for extending the survivability of restorations. Dentists, educators, and researchers will continue their search for improved technologies that detect early stages of lesion development. Improved monitoring of early carious lesions is essential to judge whether new methods and materials of disease management ensure remineralization to avoid surgical intervention. If successful, these technologies and diagnostic methods would satisfy the “proven technologies, materials, and devices” outcome of [Figure 20-1](#).

Several innovative methods for prosthesis construction in lab settings have already emerged, and others are emerging. Technology improvements related to oral and maxillofacial reconstruction methods will continue to offer pathways to improve oral health care. Meanwhile, the search will continue for biological technologies that may allow “natural or organic” regeneration of lost or diseased tissues.

This chapter may serve as a platform from which further innovative technologies for oral and maxillofacial applications can evolve with the research of materials scientists, chemists, implantologists, molecular biologists, cell biologists, and geneticists. Sustained collaboration among researchers and clinicians is essential to expedite the development, evaluation, and adoption of new technologies for improving oral health outcomes.

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Selected Readings (Web Version)

Useful Websites (Accessed May 2020)

Library of critically appraised topics related to clinical dental problems (<https://cats.uthscsa.edu/>). The “CAT” library provides key word-searchable topics. Each topic is presented as a structured one-page summary and critique of the best available evidence on a focused question. The library is designed as a rapidly accessible source of evidence-based information for use in making clinical dental decisions.

The Eco-Dentistry Association: <http://www.ecodentistry.org/?page=AboutGreenDentistry>.

Information about the association and resources to develop “green” dental practices.

Dental Restorative Materials—A Pollution Prevention Perspective: <http://wspn.org/studies/dental-chemical-use/fact-sheets/restorative-materials/>.

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