



Bioceramics in Endodontics

Edited by **Viresh Chopra**



WILEY Blackwell

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Foreword by Professor Nutayla Said Al Harthy

Clinicians today are challenged by rapidly evolving information related to clinical techniques and materials, making the process of critically appraising the available dental literature for focused, evidence-based, patient-centered care challenging. Dr. Viresh Chopra has yet again put together a reference textbook, further assisting clinicians interested in practicing contemporary endodontics to make informed decisions when using “Bioceramics in Clinical Endodontics.”

“Bioceramics in Clinical Endodontics” provides the reader with not only the information required to have a sound understanding of the subject within today’s practice of clinical endodontics. This book also includes rich illustrations and numerous clinical cases along with an accessible video clip, making it clinically focused.

Dr. Viresh Chopra and the contributors should be commended for their dedication in compiling this reference book in endodontics by covering the background and core principles in the use of bioceramics in contemporary endodontics in a clinically comprehensible and attractive format.

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Foreword by Stephen Cohen

As a professor of endodontics, I have witnessed the rapid advancements in the field of endodontics over the years. One of the most significant contributions to this field has been the emergence of bioceramics. Bioceramics have revolutionized the way we approach endodontic procedures, providing us with a more efficient and effective means of treating our patients.

This book on bioceramics as part of clinical endodontics is a comprehensive guide that covers all aspects of this exciting field. From the history and development of bioceramics to their current clinical applications, this book provides a detailed overview of this field.

The author has expertly curated a collection of chapters that cover the various types of bioceramics, their properties, and their clinical applications. Additionally, the book includes case studies that demonstrate the successful use of bioceramics in various dental procedures.

As a professor of endodontics, I highly recommend this book to anyone interested in learning more about bioceramics. This book is an invaluable resource that provides a thorough understanding of this fascinating field, and I am confident that it will serve as an excellent reference for many years.

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Preface

The first edition of this textbook includes the latest updates and recent developments in Bioceramics for clinical use in endodontics. The book provides an excellent update on the material science, characteristics, and clinical endodontic applications of bioceramics for students in graduate programs and residencies. This book presents a series of chapters focusing on the origin of dental bioceramics, their physical and mechanical properties, clinical applications, recent updates, future directions, and ideas for future research on bioceramics. In addition, clinical endodontic cases have been added to this book, which will serve as a guide to using bioceramics in various clinical scenarios that a dentist encounters in their day-to-day endodontic practice.

This book has been designed for a wide range of dental community, starting from undergraduates, postgraduates, endodontist, as well as dental practitioners who have a special love for endodontics. This is the reason why, along with didactic chapters on history and material properties, a section on clinical cases has been added to this book. In addition, this book has a companion website where the readers can enjoy videos demonstrating the use of bioceramics in various clinical cases while it is performed on patients. This will give readers a chance to apply these materials as per the protocol in their own practice using these chapters as a guide.

This book would have not been possible without the contributions from all the authors and a number of people who have worked hard on the preparation of the text. As an editor, I would like to thank Mr. Atul Ignatius David for coping with me during the entire course. I would also like to thank Ms. Rituparna Bose and Susan Engelken for their continuous follow-ups. Many thanks to the entire WILEY team for their support in bringing out this version of the book.

This book should be of interest to researchers, graduate students, postgraduates, and private dental practitioners. It should serve as a useful reference for material scientists and dentists with an interest in bioceramics and

performance of the dental engineered material. We hope that the broader spectrum of this book will facilitate the exchange of information between a wide range of dental professionals and also serve as a reference for further research ideas on Bioceramics.

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“Real dream is not what we see in sleep but which does not allow us to sleep”

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About the Companion Website

This book is accompanied by a companion website.

www.wiley.com/go/chopra/bioceramicsinendodontics

This website includes Videos



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Bioceramics in Dentistry

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1.1 Introduction

Biomaterials as described by the American National Institute of Health are natural or synthetic substance(s) other than drugs that can be used for therapeutic or diagnostic medical purposes to maintain or improve the quality of life[1]. Along with biocompatibility, biological sustainability is also a very important property of any biomaterials that are intended to be used to reconstruct body function for an unspecified duration. However, materials are also required for temporary support of functions. Therefore, depending on the tissues to be replaced and function required, different types of materials are used as a biomaterial, e.g. metal, ceramic, polymer, hydrogel, or composite.

Ceramics are inorganic, non-metallic materials that are hard, brittle, heat-resistant, and corrosion-resistant. In addition to their biocompatibility, ceramics can be obtained with biostable, bioactive, or bioresorbable properties making them eligible to be used as biomaterials. Ceramic base biomaterials that are specially developed for biological applications (both medical and dental)

are categorized as Bioceramics. Porous bioceramics (BC) can facilitate neo-angiogenesis and neo-osteogenesis inside their porous structure. Additionally, resorbable bioceramics get replaced by the newly formed desired tissues.

Josette Camilleri described bioceramics in endodontics as the materials that are composed of tricalcium silicate-based cement synthesized from lab-grade chemicals and that do not include aluminum in their composition [2].

1.2 History and Evolution of Bioceramics

- Portland cement that was obtained from the limestones coming from Portland got patented in 1824 [3, 4].
- According to Peltier, the use of plaster of Paris, a resorbable ceramic, was first described by Dressman in 1892 to fill the bone cavities which were later found to be filled with solid bone [5].
- In the early 1920s, the use of calcium phosphates as a stimulus to osteogenesis for bone defect repair started [6].
- Use of ceramic hydroxyapatite (HA) granules for bone defect repair was first reported in the early 1950s [7].
- In 1963, Smith worked on a ceramic bone substitute, Cerosium [8].
- In 1969, researchers found a new material called bioglass that could be easily integrated into human bone [9].
- In the 1980s, the first hydroxyapatite coated implants were marketed.
- LeGeros et al. in 1982 used calcium phosphate in restorative dental cement as a bioceramics material [10].
- In 1984, the use of bioceramics started as a root canal sealer [11].
- The first self-hardening calcium phosphate cements (CPCs) were developed in 1986 [12].
- MTA was developed in the Loma Linda University, California, and was first documented in 1993 [13, 14] as a retrograde filling and perforations repair material.
- Chevalier et al. in 1997 found that the friction between zirconia and alumina is very low.
- In 1998, “TH-Zirconia” implants were introduced.
- The United States witnessed the first commercial MTA product, ProRoot MTA (Dentsply Tulsa Dental Specialties, Johnson City, TN) in 1999.
- In 2009, Septodont, France, marketed the calcium silicate-based product “Biodentine” as a permanent bulk dentin substitute.
- Angelus was the first company to launch a paste/paste bioceramic root canal sealer (MTA-Fillapex) in 2010.
- In 2019, Bio-C® Temp, a ready-to-use bioceramic paste for intracanal dressing was developed by Angelus, Brazil.

Earlier in the 1950s, bioceramics were used in dentistry because of their inertness and good biocompatibility that had no reaction with living tissues, e.g. zirconia, alumina, and carbon. They were primarily used for the fabrication of dental implants and prosthesis. Later on, the development of bioactive ceramics, e.g. bioglass (45S5) by Hench [9], extended the scope of these bioceramic materials as they offered in vivo benefits by inducing biomineralization (i.e. formation of apatite crystal layer). Bioglass (45S5) is composed of 45% SiO_2 , 24.5% CaO , and 24.5% Na_2O . The addition of 6% P_2O_5 by weight enhanced the bioactivity of the glass [15]. However, this glass material was very weak and brittle. In the 1980s, the trend changed toward using implant ceramics that react with the environment and produce newly formed bone.

This bioglass was later modified to create variants by adding magnesium, borates, etc., for improving mechanical and setting properties of bioceramics [3].

Acknowledging the bioactivity property of bioceramics and their application into dentistry as mineralizing and regenerative materials has brought enormous productive changes [16].

Bioactive materials such as sintered hydroxyapatite (HA) [17] and β -wollastonite (CaO-SiO_2) in an MgO-CaO-SiO_2 glass-based matrix [18, 19] have been developed for over the last four decades [20].

Ternary CaO-MgO-SiO_2 system-based glass ceramics possessed better mechanical and chemical properties and thus are suitable materials for wear resistance, biomedical, and ceramic coating applications [21–23]. The addition of fluorides of Ca and Mg to substitute Na_2O in the conventional composition ($\text{SiO}_2\text{-CaO-Na}_2\text{O-P}_2\text{O}_5$) led to the development of antibacterials and bioceramics with higher flexure strength and hardness [20]. Ion substitutions (Ca^{2+} , Mg^{2+} , and B^{3+}) decreased the coefficient of thermal expansion of the bioactive glass ceramics [19]. In addition to bioglass, calcium silicate and aluminate based bioceramics also showed the property of biomineralization.

Although the shift from older to newer formulations is quite slow, many bioceramic materials have been developed that overcome the previous drawbacks.

1.3 Classification of Bioceramics

Bioceramics are classified on the basis of their generations, interaction with tissues, structure, composition, resorbability, and uses.

1.3.1 Based on Generations

Bioceramics are divided into three generations:

- 1) First generation: The first generation bioceramics are inert, thus do not initiate any reaction with living tissues, e.g. zirconia and alumina. Although they are biocompatible, for the body tissue they are like a foreign body,

leading to the formation of an acellular collagen capsule which isolates them from the body tissues.

- 2) Second generation: In the 1980s, the trend changed toward the development of bioceramics with improved bioactivity and the second generation bioactive bioceramics were developed, e.g. calcium phosphates, glasses and ceramic glasses, and calcium silicate. These bioceramics can react with the physiological fluids forming biological-type apatite as a byproduct of said reaction; in the presence of living cells, this apatite can form new bone.
- 3) Third generation: The third generation bioactive, porous bioceramics were developed because of biological requirements. Only porous ceramics can fulfil physiological requirements in their use as scaffolds for cells and inducing molecules and being able to drive self-regeneration of tissues. Example: nanometric apatites, shaped in the form of pieces with interconnected and hierarchical porosity, within the micron range so that cells can perform their bone formation and regeneration tasks.

1.3.2 Based on Tissue Interaction

The fact that the reactivity of solids begins on their surface is of particular importance in the field of bioceramics because on application they remain in contact with an aqueous medium and in the presence of cells and proteins [24]. Based on different types of interactions [25, 26] shown by bioceramics, it is classified as:

- 1) Bioinert: These materials have a high chemical stability *in vivo*; thus, they do not interact and show no chemical changes when they are in contact with living tissues. They also possess high mechanical strength, e.g. alumina, zirconia, and carbon.
- 2) Bioactive: Bioactive bioceramics have the character of osteoconduction and the capability of chemical bonding with living bone tissue. These materials bond directly with living tissues by undergoing interfacial interactions, e.g. bioactive glasses, HA, calcium silicates, and calcium aluminates.
- 3) Biodegradable: These materials when in contact with living tissues either become soluble or resorb and eventually get replaced or incorporated into tissue, e.g. tricalcium phosphate, calcium phosphate, aluminum–calcium–phosphates, and calcium aluminates.

1.3.3 Based on Structure

Depending on the structure type, bioceramics are classified into:

- 1) Dense: Bioceramics that are available as solid bulk structures like bars, rods, or to any shape through injection molding fall in this category. Because of their nonporous nature, these bioceramics show poor vascularization and osteoinduction ability, e.g. zirconia.

- 2) Porous: Porous bioceramics have attracted tremendous attention with their excellent biological function and osteoinduction ability. They provide scaffolds for cells to adhere, proliferate, differentiate, and regenerate tissues. The mean size and surface area of porosity plays an important role in the growth and migration of a tissue into the bioceramic scaffolds, e.g. CaP scaffold.

1.3.4 Based on Composition

On the basis of their composition, bioceramics are classified into:

- 1) Calcium silicate-based: The calcium silicate-based bioceramics can be further categorized on the basis of their application:
 - a) Cement: e.g. Biodentine (Septodont, France), mineral trioxide aggregate (MTA), Portland cement.
 - b) Sealer: BioRoot RCS (Septodont, France), Endo-CPM-Sealer (EGO SRL, Buenos Aires, Argentina), MTA Fillapex (Angelus, Brazil), TECHBiosealer (Profident, Kielce, Poland).
- 2) Calcium phosphate-based bioceramics: These materials are obtainable as bone cements, paste, scaffolds, and coatings. The tricalcium phosphate has shown the property of osteogenesis during bony defect treatment, e.g. tricalcium phosphate and HA. Bioglass, a glass ceramic containing calcium and phosphate, showed bonding with the living bone with a calcium phosphate-rich layer [27].
- 3) Mixture of calcium silicates and calcium phosphates: EndoSequence BC Sealer (Brasseler, Savannah, GA, USA)/Total Fill, BioAggregate (Innovative Bioceramix Inc., Vancouver, Canada), Tech Biosealer, Ceramicrete (developed at Argonne National Lab, IL, USA), iRoot BP, iRoot BP plus, iRoot SP (Innovative Bioceramix Inc., Vancouver, Canada)
- 4) Calcium aluminate-based: These materials can set, harden, and maintain their physical and mechanical properties over time in an oral environment. They have the ability to create apatite on their surface and provide tight seal between the tooth and itself. The cements can also contribute to the healing of the dental pulp or in the tissue surrounding the root of a tooth by eluting ions to stimulate cytokines, e.g. EndoBinder, GenereX, Capasio, and Quick-set.

1.3.5 Based on Resorbability

- 1) Nonresorbable: Alumina, zirconia, carbon, HA, and calcium phosphate cement.
- 2) Resorbable: β tricalcium phosphate and calcium sulfate

1.3.6 Based on Their Location-Specific Use in Endodontology

They are classified as [28]:

- 1) Intracoronar
 - Pulp capping materials
 - Regenerative endodontic cements
- 2) Intraradicular root canal sealers
 - Apical plug cements
 - Perforation repair cements
- 3) Extraradicular
 - Root-end filling materials
 - Perforation repair cements

1.4 Forms of Bioceramics

Bioceramics are available in different forms and phases:

- Powder or microspheres
- As a thin coating on a metal or polymer
- Porous 3D structure
- Composites with a polymer component
- Solid dense structure.

1.4.1 Alumina

Aluminum oxide (Al_2O_3) is commonly known as alumina. It is highly inert and resistant to corrosion even in a highly dynamic oral environment. Additionally, it has high wear resistance and surface finish. As an implant material, it was first used in the 1970s. It does not integrate with bone or soft tissues. Because of its hardness being higher than the other metal alloys, alumina found its main application as biomaterials in the articular surfaces of joint replacements [29].

1.4.2 Zirconia

Zirconium dioxide is commonly known as zirconia. As zirconium is a very strong metal, it is also known as “ceramic steel.” The inherent properties of zirconia such as inertness, high toughness, strength, wear resistance, fatigue resistance, and biocompatibility make it suitable to be used as dental bioceramics.

Zirconia established itself as implant material in the 1960s. Compared to zirconia, partially stabilized zirconia showed superior flexural strength, fracture toughness, lower stiffness, and a superior surface [30].

1.4.3 Hydroxyapatite (HA)

HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is a major component of human bones and teeth. It belongs to the calcium phosphate family with a calcium to phosphorus ratio of 1.67. Since most of the inorganic portion of the human bone tissue is HA, it can be effective in reconstructing human bone tissue. It is capable of integrating and supporting bone growth, without breaking down or dissolving. It has higher stability in aqueous media than other calcium phosphate ceramics within a pH range of 4.2–8.0 [31]. In the 1970s, resorbed residual ridge repair started with HA and in 1988 in North America it was declared as a successful implant material.

To fill the bone defects or spaces, HA may be used in the form of either powder, blocks, or beads. The bone filler acts as a scaffold to facilitate the formation of natural bone.

HA is also used to alter the surface properties of metals by the application of coating on its surface. Because of the poor mechanical properties, HA cannot be used for load-bearing applications.

1.4.4 Calcium Phosphate

Examples of calcium phosphate-based bioceramics used in dentistry are CPC, tricalcium phosphate, HA, and bioglass that are used as bone substitutes and also an adjunct with the dental cements [25]. CPC offers the potential for in situ molding and injectability.

Tricalcium phosphate is a biodegradable bioceramic. Tricalcium phosphate has four polymorphs; the most common ones are the α and β forms. It dissolves in physiological media and can be replaced with bone during implantation.

When the ratio of Ca/P in calcium phosphate compounds is less than 1, it becomes highly soluble and is thus unsuitable for biological implantation. It is used as a coating on metallic implants, as fillers in polymer matrices, as self-setting bone cements, as granules or as larger shaped structures.

1.4.5 Mineral Trioxide Aggregate

Dr. Torabinajed introduced MTA in 1993. MTA powder comprises 75% mixture of tricalcium silicate $(\text{CaO})_3\text{SiO}_2$, dicalcium silicate $(\text{CaO})_2\text{SiO}_2$, and tricalcium aluminate $(\text{CaO})_3\text{Al}_2\text{O}_3$ 20% bismuth oxide; and 5% gypsum. This combination

possesses osteoconductive, osteoinductive, and biocompatible properties. When mineral trioxide powder is mixed with water, initially calcium hydroxide and calcium silicate hydrate are formed [32]. MTA is an active biomaterial with the potential to interact with the fluids in the tissues. The pH value is 10.2 after mixing and it rises to 12.5 at three hours resulting in an alkaline environment [32].

1.4.6 Biodentine

Biodentine, a tricalcium silicate-based hydraulic cement, was developed by Septodont research group (Septodont, Saint-Maur-des-Fosses, France) as a bio-active dentin substitute material. Tricalcium silicate is the main component and the additives include calcium carbonate in the powder; calcium chloride, water-soluble polymer, and water make the liquid. Calcium chloride controls the setting time. Biodentine exhibits a higher initial rate of calcium ion release compared to other similar material types [33, 34]. This is due to the interaction of the calcium carbonate that enhances the reaction rate [35].

Hydrated calcium silicate gel and calcium hydroxide are produced because of the hydration of tricalcium silicate. The hydrated calcium silicate gel and calcium hydroxide gradually fill in the spaces between the tricalcium grains by precipitating at the surface of the particles. Biodentine continues to improve in terms of internal structure toward a denser material, with a decrease in porosity after the initial setting.

1.5 Physicochemical Properties of Bioceramics

The physiochemical properties of bioceramics govern the application and outcome of the use of bioceramic materials. The therapeutic effect of these biomaterials in aiding healing and restoring function is dependent on the chemical reactions that affect their setting, hardening in the presence of oral tissues and fluids. The biological response of the tissues is mediated through a dynamic interaction between these materials, depending on their composition, biocompatibility, and specific properties such as surface microhardness, flow, pH, flexural strength, etc. related to them. The following discussion is focused on the physicochemical properties of commercially used bioceramics commonly used in endodontics.

1.5.1 Portland Cement

Portland cement (PC) offers antibacterial activity, biocompatibility, bio-inductivity, and acceptable physical and chemical properties when used for varied