PHYSICAL, MECHANICAL AND ENVIRONMENTAL PROPERTIES OF DENTAL RESIN COMPOSITES BASED ON HYDROXYAPATITE FILLED BIS-GMA/TEGDMA

By

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LIST OF SYMBOLS

p	: Density
p_c	: Density of composite
p_f	: Density of filler
W_d	: Dry weight of samples
L	: Load
W_m	: Saturated weight of samples
S	: Span length
w	: Specimen width
b	: Specimens thickness
W_s	: Suspended weight of samples
m	: Tangent gradient of the initial straight line.
v_f	: Volume fraction
w_f	: Weight fraction of filler
w_r	: Weight of resin composite ash
w_0	: Weight of resin composite specimen
a	: Notch length
d	: Average length of indented diagonals
f	: Geometric correction factor
K_{IC}	: The stress intensity factor
m_1	: Conditioned mass, in µg, prior to immersion in water.
m_2	: Mass of the specimen, in µg, after immersion in water
m_3	: Reconditioned mass of the specimen, in µg after dry
v	: Volume of the specimen, mm^3
γ-MPS	: 3-(trimethoxysilyl)propyl methacrylate
µg	: microgram
µm	: micrometer

LIST OF ABBREVIATIONS

ASTM : american society for testing and material
BIS-GMA : Bisphenol A-glycidyl dimethacrylate
CQ : Camphorquinone
DMAEMA : Dimethylaminoethyl Methacrylate
DSC : Differential Scanning Calorimetry
DTG : Differential thermogravimetry
FESEM : Field Emission Scanning Electron Microscope
FTIR : Fourier Transform Infra red spectroscopy
HA : Hydroxyapatite
ISO : International Standards Organization
LED : Light-Emitting Diode
OD : Optical Density
PAC : Plasma-Arc
PMMA : Poly (methyl methacrylate)
PVC : Polyvinyl Chloride
QTH : Quartz-Tungsten Halogen
SBF : Simulated Body Fluid
SEM : Scanning Electron Microscopy
SENB : Single-Edge Notched Bending
SiC : Silicon Carbide
TEGDMA : Triethyleneglycol dimethacrylate
TGA : Thermogravimetric Analysis
VH : Vickers Hardness
VLC : Visible Light-Curing

SIFAT-SIFAT FIZIKAL, MEKANIKAL DAN PERSEKITARAN KOMPOSIT RESIN GIGI BERASASKAN BIS-GMA/TEGDMA TERISI HIDROKSIAPATIT

ABSTRAK

Komposit resin gigi (tampalan putih) disediakan dengan mencampurkan hidroksiapatit (HA) sebagai pengisi ke dalam monomer bisfenol A-glisidil dimetakrilat (Bis-GMA) berkelikatan tinggi. Monomer Bis-GMA ini dicampur secara mekanikal dengan monomer trietilena glikol dimetakrilat (TEGDMA) berkelikatan rendah sebagai monomer pencair, kamforkuinon (CQ) digunakan sebagai pemula manakala dimetil amino etilmetakrilat (DMAEMA) digunakan sebagai pemecut. Zarah-zarah HA dirawat dengan agen pengganding silana 3-(Trimetoksilil) propil metakrilat (γ-MPS) sebelum ia dicampur ke dalam Bis-GMA /TEGDMA. Kesan γ-MPS ke atas permukaan dan morfologi pengisi masing-masing telah dikaji menggunakan Transformasi Fourier Inframerah (FTIR) dan Mikroskop Elektron Pengimbas (SEM). Tiga nisbah berbeza untuk HA yang dirawat iaitu 40, 50 dan 60 wt.% telah dicampurkan ke dalam Bis-GMA /TEGDMA. Campuran ini diacu manakala pempolimeran sampel dilakukan menggunakan sistem pempolimeran cahaya nampak (VLC) dengan masa penyinaran selama 60 saat dari kedua-dua bahagian. Sampel-sampel ini diuji untuk mengetahui sifat-sifat fizikal, mekanikal, terma, dan persekitarannya. Hasil kajian menunjukkan bahawa ketumpatan Bis-GMA /TEGDMA meningkat selari dengan pertambahan kandungan pengisi yang dianggap sesuai untuk kegunaan pergigian. Selain itu, peningkatan kandungan pengisi telah mengurangkan lagi ciri-ciri keliatan patah (K_{IC}) dan kekuatan lentur. Sebaliknya, peningkatan kandungan pengisi telah meningkatkan lagi modulus lentur dan kekerasan permukaan. Kestabilan terma Bis-GMA/TEGDMA berisi HA dinilai menggunakan analisis termogravimatrik (TGA) dan kalorimetri imbasan beza (DSC). Peningkatan beban pengisi ke dalam Bis-GMA/TEGDMA telah meningkatkan kestabilan terma. Penilaian sifat-sifat persekitaran menunjukkan bahawa penyerapan dan keterlarutan di dalam air serta bendalir tubuh tersimulasi (SBF) bagi kesemua formulasi telah berkurangan dengan ketara dengan meningkatnya beban pengisi. Kesan pendedahan air terhadap keliatan patah dan kekerasan permukaan menunjukkan bahawa kedua-dua ciri tersebut telah berkurangan selepas sampel-sampel direndam di dalam air. Akhir sekali, radiopasiti Bis-GMA/TEGDMA berisi HA dipertingkatkan dengan pertambahan kandungan pengisi. Komposit yang mengandungi 60 wt.% zarah-zarah HA mempunyai ketumpatan optik yang hampir sama dengan ketumpatan optik plat aluminium yang berketebalan sama.

PHYSICAL, MECHANICAL AND ENVIRONMENTAL PROPERTIES OF DENTAL RESIN COMPOSITES BASED ON HYDROXYAPATITE FILLED BIS-GMA/TEGDMA

ABSTRACT

Dental resin composite (white filling) was prepared by incorporating hydroxyapatite (HA) as filler into high viscosity monomer bisphenol A-glycidyl dimethacrylate (Bis-GMA). Bis-GMA monomer was mixed mechanically with a low viscosity monomer triethyleneglycol dimethacrylate (TEGDMA) as diluent monomer, camphorquinone (CQ) was used as initiator and dimethylaminoethyl methacrylate (DMAEMA) was used as accelerator. HA particles were treated with silane coupling agent 3-(Trimethoxysilyl) propyl methacrylate (γ-MPS) before incorporating into Bis-GMA/TEGDMA. The effect of γ-MPS on the surface and morphology of the filler was studied using Fourier Transform Infrared (FTIR) and scanning electron microscopy (SEM), respectively. Three different ratios of treated HA i.e. 40, 50 and 60 wt.% were added into Bis-GMA/TEGDMA. The mixture was moulded and the polymerization of the samples was carried out using a visible light curing (VLC) system with an irradiation time of 60 sec from both sides. The samples were tested for physical, mechanical, thermal and environmental properties. The results showed that the density of Bis-GMA/TEGDMA increased with the increase of the filler loading which is considered appropriate in dentistry use. Additionally, the increase of filler loading resulted in the decrease of fracture toughness (K_{IC}) and flexural strength values. By contrast, the increase of filler loading resulted in the increase of flexural modulus and surface hardness. The thermal stability of HA filled Bis-GMA/TEGDMA was evaluated using thermogravimatric analysis (TGA) and differential scanning calorimetry (DSC). The increase of filler loading into Bis-GMA/TEGDMA resulted in the improvement of thermal stability. Environmental properties evaluation revealed that the absorption and solubility in water and simulated body fluid (SBF) of all formulations were reduced significantly with the increase of the filler loading. The effects of water exposure on the fracture toughness and surface hardness showed that both properties decreased after the samples were immersed in the water. Finally, the radiopacity of HA filled Bis-GMA/TEGDMA was improved with the increase of the filler loading. The composite containing 60 wt.% of HA particles had optical density close to the optical density of aluminum plate of the same thickness.

CHAPTER 1

INTRODUCTION

1.0 Introduction

Research and development in dental resin composite "Dental white filling" was initiated in the 1960s. A resin matrix and filler materials are the components of a dental resin composite. As they lack enough strength to withstand the pressure and wear generated by the posterior teeth, the use of dental resin composites was restricted to the anterior teeth. Restorative dental materials should have mechanical properties analogous to those of enamel and dentin (Willems et al., 1992).

The life span for posterior resin composite restorative is often not longer than 2-4 years but for anterior polymeric restorative materials is about 8 years (Sideridou et al., 2002). Moreover, a latest reconsideration of longitudinal clinical studies validated that bulk fracture of the composite was the most frequent cause for restoration replacement after 5 years (Brunthaler et al., 2003), which is regarded as a very short period of time when compared with traditional dental amalgams, which have lifetime of about 10-20 years (Bogdal et al., 1997). Consequently, dental resin composites have considerably advanced in strength and can be utilized effectively for the back teeth. Dental resin composites are used for cosmetic improvements to the teeth by giving a natural colour as well as for restoring decay and filling small cavities.

As a result of technological progress in material strength, it has become possible to replace larger cavities with resin composite. Preferably, too large of a cavity is best treated with another material such as a dental crown. Resin composite can be used as a cosmetic breakthrough in dentistry. In the past, dentists could only set silver or gold fillings in all cavity preparations; however, nowadays patients could select a more pleasing and natural filling material. Dental resin composites adhere to teeth which helps maintain and isolate the remaining tooth structure. The bonding technique allows preservation of tooth structure. The dentist, when placing dental composite, no longer relies on internal characteristics of the tooth to hold a filling in place. Instead, resin composites are directly joined to the tooth. Dental amalgam or "Silver filling" rely on internal features of a tooth to hold it in place.

Considerable numbers of studies have been carried out to probe the polymerization, filler phases, resin compositions, and mechanical properties of resin composite. To improve the dental resin composite properties, many methods have been studied such as: reinforcement with chopped glass fibers, networked fibers, and optimization in filler level and degree of conversion. It is recognized that the mechanical characteristics of dental resin composites depend on particle size of filler. Therefor, the size of the filler particles in dental resin composite materials has been reduced considerably in the last decades, where it ranged between 0.7-3.6 µm for modern small-particle composites (Willems et al., 1992). An important reason for declining the filler particle size is the difficulty encountered when polishing coarse particle composites. The difference in hardness of the inorganic filler particles and the resin matrix causes rough or dull surfaces. Consequently, traditional resin composite restorations produced increase plaque retention and gingival irritation. Furthermore, these restorations were sensitive for staining (Tjan and Chan, 1989).

Dental resin composite is reinforced with inorganic fillers to concentration up to about 70 wt.%. Though the types of fillers vary, most of them comprise short glass fibers, silica and ceramic particles or whiskers (Xu et al., 1999). However, additional major upgrading is needed for the purpose of extending the use of resin composites to large stress-bearing applications such as direct posterior restorations involving cusps.

1.1 Problem statement

Bisphenol A-glycidyl dimethacrylate (Bis-GMA) was discoverd in early 1960s and it is the most extensively utilized as base monomer of resin composite restoration since it was discoverd, dimethacrylate networks have been broadly applied in dentistry in crown and bridge prostheses, pit and fissure sealants, and tooth restorative composites. The extra time required to place posterior resin composite restorations was consumed by adhesive bonding steps, shaping and polishing with rotary instruments, and control of moisture. Moisture contamination during posterior resin composite placement could not be tolerated, and thus demanded a higher fee (resin composite fillings are usually more costly than dental amalgam fillings) (Sarrett, 2005). Moreover, the lifetime of the dental amalgam is longer than resin composite since the later possess relatively poor wear resistance. In addition, the low fracture toughness of many resin composites is one of the factors that reduce the utilization of these materials for posterior restorative purposes (Wilson et al., 1997). Applying dental resin composite for large restorations is still controversial and fracture of restorations in the posterior region has been found to be a frequent cause for restoration failure (Opdam et al., 2004). Several authors have established limits for the utilization of resin composite in the posterior region, restricting their use to small cavities. In reality, dental resin composite restorations must endure harsh environment that varies from patient to patient. There are many uncontrollable factors that affect composite restoration longevity including occlusal habits, chemically active foods and liquids, abrasive foods, temperature fluctuations, humidity variation, mastication forces, bacterial byproducts, and salivary enzymes (Sarrett et al., 2000). Yet, in aqueous environment they suck up water and release unreacted monomers. The release of uncured monomers from resin composite may stimulate the growth of bacteria around the restoration (Hansel et al., 1998), and promote allergic reactions in some patients (Spahl et al., 1994). Furthermore, the water ingress into dental resin composite in the oral cavity can with time, result in degradation of the physical and mechanical properties (Söderholm et al., 1984).

The focal research approach for enhancing and improving the physical, mechanical, thermal and environmental properties of dental resin composite is via the incorporation of hydroxyapatite (HA) powder to function as reinforcement. It is broadly used as biomaterials due to its biocompatibility and higher wear resistance, particularly since it pioneered the use of hydroxyapatite to strengthen high density polyethylene for bone substitutes (Bonfield et al., 1981). Additionally, it does not cause toxic reactions like foreign body giant cell reaction (Costantino et al., 1993 & Mohamed, 2006). Another approach was filler surface treatment by exploiting 3-(Trimethoxysilyl) propyl methacrylate (γ-MPS) as the silane coupling agents to improve the mechanical stability of the filler-matrix interface, and increase the strength and hardness of composite resins. However, the manipulation of hydroxyapatite in dental resin composite as reinforcement is not widely testified.

1.2 Research objectives

The objectives of this research are to fabricate a new dental resin composite based on of bisphenol A-glycidyl dimethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA). These two materials constitute a good combination of dental resin composite. The microscopic particles of bioceramic filler HA will be applied in preparing the dental resin composite. The study will examine the effects of the filler loading on the physical, mechanical, thermal and environmental properties of Bis-GMA/TEGDMA. Moreover, it will determine the influence of chemical treatment of HA surface using silane coupling agent for further enhancement of the composites properties. Thus the objectives of the research are:

i. To study the effect of HA loading on the physical, mechanical and thermal properties of the Bis-GMA/TEGDMA.
ii. To study the influence of HA loading on the environmental properties such as water and simulated body fluid (SBF) absorption, and solubility in water and simulated body fluid (SBF) on the performance of the Bis-GMA/TEGDMA.
iii. To study the mechanical properties of the HA filled Bis-GMA/TEGDMA due to water exposure.
iv. To study the effect of HA loading on the radiopacity of the Bis-GMA/TEGDMA.

1.3 Organization of the thesis

The thesis comprises of five chapters. The contents of each chapter are briefly described as follows:

Chapter one provides a brief introduction to dental resin composite and the lifetime of polymeric restorative. The objectives and the general lay out of the whole research program are underlined.

Chapter two is a literature review, which presents an overall background of the thesis. It gives common concepts and relevant research related to this work.

Chapter three specifies step-by-step experimental procedures utilized in this research. It also illustrates descriptions of laboratory equipments utilized as well as any other processing techniques used in producing data that were used and offered in this research.

Chapter four provides the results and discussion of the present research. It begins with explanations on the filler partical size and filler partical size distrbtion and effects of silane coupling agents on the surface of the HA filler. FTIR and SEM were also presented in this chapter to characterize the surface of treated fillers. The effect of HA filler loading on the density of the Bis-GMA/TEGDMA was determined. Further, the results on the effect of HA filler loading on the mechanical, thermal and environmental properties of the Bis-GMA/TEGDMA are also presented and discussed. As a final point, the findings of the effect of HA loading on the radiopacity of Bis-GMA/TEGDMA are examined.

Finally the conclusion, recommendations of this research, and some suggestions for future research make the contents of chapter five.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

To begin with, there are different kinds of dental materials that have been utilized as tooth crown and root substitutions such as: animal teeth, seashells, human teeth, ivory, ceramics, bone and metals. Restorative materials to substitute the missing part of tooth structure have advanced slowly over the past few centuries. An ideal restorative material would be biocompatible, attach enduringly to tooth structure or bone, harmonize the natural appearance of tooth structure and other visible tissues, display properties compatible to those of tooth enamel, dentin, and other tissues, and has the ability of commencing tissue restoration or regeneration of missing or spoiled tissues. The dental matreials which are used to replace missing part of tooth structure are exposed to attack by temperature and aqueous environment of oral cavity and are also subjected to biting forces. Furthermore, the restorative dental materials are cleansed and polished by various materials. Thus, understanding the physical, mechanical and environmental properties of the materials using in dentistry is very important.

This chapter provides an overview of dental materials. Firstly, the historical use of dental materials is illustrated with particular focus on the developments in this field over the years. The later part provides introduction to biomaterials including their major advantages and disadvantages followed by various types of biomaterials used in dentistry with special focus on recent advances in the use of synthetic biomaterials. The application of various biomaterials and their properties are also described. The topic on restorative dental material, as a part of dental materials, is explained in more detail. Besides, the composites as a part of dental restorative materials are also elucidated. The last section reviews some of properties of dental restorative materials.

2.1 The use of dental materials - A historical perspective

Teeth cavities have been substituted or repaired since ancient times to the 18th century with different kinds of materials such as ivory, human teeth, stone chips, gums, turpentine resin, cork, and metal foils (lead and tin). In recent times, specialists have utilized gutta percha, cements, unfilled synthetic resin, composites, metal-modified cements, other metals (amalgam, gold leaf, and a mixture of cast metals and alloys), metal-ceramics, and ceramics for tooth restoration (Anusavice, 2003).

For filling tooth cavities, Fauchard (1678-1761), who is considered as the father of the modern dentistry, used tin foil or lead cylinders. Modern dentistry began in 1728 with the publication of a treatise by Fauchard. The treatise tackled the different types of dental restorations such as a method for construction of artificial denture made from ivory. As a foil, gold was also used for dental restorative purposes. This gold foil was used by Pfaff (1715-1767) to cap the pulp chamber. Pfaff in 1756 also experimented a method for making impressions of the mouth in wax. Later, he created a model by using plaster of Paris. In 1774, a model was designed by Dachateau, a French pharmacist and de Chemant, a dentist for producing hard, decay-proof porcelain dentures. In 1789, de Chemant found out an improved version of these "mineral paste" porcelain teeth (Anusavice, 2003).

The creation of the first dental amalgam, called silver filling was in France in the early years of the 18th century while it spread to the United States (US) in about 1830, and at about the same time, porcelain teeth were introduced in America (Ferracane, 2001). After that, the porcelain inlay was invented in the early 1800s (Anusavice, 2003). With the coming of the 1850s, plaster was utilized to make impression, gutta percha was discovered as the filling of root canals and gold and platinum-based metal mixtures came into use, the hard rubber material called vulcanite was also utilized as a substitute for ivory dentures, and zinc oxychloride compound gradually began to be used as cementing agent and restorative. By the end of the 18th century, zinc phosphate and silicate cements appeared for saving circular gold inlays into prepared cavities (Ferracane, 2001). In 1907, the detached-post crown became adjustable (Anusavice, 2003).

By 1935, polymerized acrylic resin was introduced as a denture base material to back up artificial teeth (Anusavice, 2003). These polymers have an important role in human life. By the end of the 1950s, other materials came into use, such as stainless steels for orthodontics, non-noble metals for casting use, elastic impression materials, and dental composites were used with the acid-etch method (Ferracane, 2001).

In 1955, Buonocore brought about the method of acid conditioning of dental structures by using phosphoric acid on enamel surface. In 1956, the use of acid on dentin surface in order to improve adhesion of restorative materials was introduced. After developing Bis-GMA molecule by Bowen (1963), the studies concerning dental bonding were conducted again. Acid conditioning of enamel was admitted to be a common procedure (Matos et al., 1997). In the 1960s, dental composites were devoted to the front teeth because they were vulnerable and unable to tolerate the pressure caused by the back teeth. Subsequently, dental composites were improved greatly (Alsharif et al., 2010a).

In the 1970s, glass ionomer and polycarboxylate cements were developed and made known. By the coming of the 1980s further advances were made in dentin adhesives, composites and ceramics. In addition, light-cured liners and glass-ionomer, sealants for the surfaces of restorations, and further alterations to orthodontic wires were introduced (Ferracane, 2001).

2.2 Biomaterials

This term refers to materials that form part of medical implants, disposables, and extracorporeal means that have been used in medicine, dentistry, veterinary medicine and surgery in addition to every aspect of taking care of patient health (Dee et al., 2002). They are further defined as “a material intended to interface with the biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body” (Williams, 1992). The biomaterial has formally defined by the Clemson University Advisory Board to be “a systemically and pharmacologically inert substance designed for implantation within or incorporation with living systems” (Wong and Bronzino, 2007). Another definition is “the materials that are biocompatible can be considered as biomaterials and the biocompatibility is a descriptive term which indicates the ability of a material to perform with an appropriate host response, in a specific application” (Black and Hastings, 1998).

There are different divisions of dental biomaterials such as natural tissues and synthetic products that can be utilized in restoring damaged, decayed or fractured teeth. Bone, dentin and enamel are types of the natural dental tissues. There are several synthetic dental material groups, such as polymers, metals, ceramics and composites. Each type of synthetic dental material has disadvantages and advantages in properties. Table 2.1 shows some examples of synthetic biomaterials for use in the body (Wong and Bronzino, 2007).

Table 2.1 Examples of synthetic biomaterials for use in body (Wong and Bronzino, 2007).

Material	**Disadvantages**	**Advantages**	**Examples**
Polymer (polyamide, silicone rubber, polyester, polytetrafuoroethylene)	Not strong, deform with time, may degrade	Resilient, easy to fabricate	Sutures, blood vessels, hip socket, ear, nose, other soft tissues.
Metals (Titanium, stainless steels, Aurum and Platinum)	May corrode, dense, difficult to make	Strong, tough, ductile	Joint replacements, bone plates and screws, dental root implants, pacer and suture wires
Ceramics (aluminium oxide, calcium phosphates including hydroxyapatite, carbon)	Brittle, not resilient, difficult to make	Very biocompatible, Inert strong in compression	Dental, femoral head of hip replacement, coating of dental and orthopedic implants
Composites (carbon-carbon, wire or fiber reinforced bone cement)	Difficult to fabricate	Strong, tailor-made	Joint implants, heart valves

2.3 Types of synthetic biomaterials

Different materials came into use in dentistry recently, like metals, polymers, ceramics, and composites.

2.3.1 Metals

The term metals refers to the metallic elements that possess the characteristic, including high thermal and electrical conductivity, opacity, ductility, luster, relatively high strength and generally melt at the high temperature (Ferracane, 2001).

Metals are considered as the oldest elements that have been used in dentistry and as structural components for mending or replacing a tooth structure due to their strength, stability and be easily formed. There are also other uses of metals, such as making crowns to substitute the outer coronal structure of a tooth, specifically in the posterior region of the mouth where the metallic colour is less objectionable. Hence, this type of restoration is referred to as an inlay. It is also called an onlay when more cusps are involved in the restoration process and when entire crown is not replaced (Ferracane, 2001). Another type of metals is called mercury. In its normal condition, mercury is a liquid at room temperature. It has been used in dentistry for restoration of damaged teeth. The mixture of mercury and particles of silver, copper and tin are used to make a hard restorative material which is referred to as amalgam. Gold is considered one of the important metals that were utilized in dentistry due to its high resistance to corrosion and tarnish. Pure gold was used to make the first cast inlay, but it was not that strong to make stress bearing restorations. So, gold was mixed with copper to support its resistance (Ferracane, 2001).

2.3.2 Polymers

The early begining of 20th century witnessed the first polymers made by man. Polymers like ceramics are characterized by being huge, long-chain organic molecules, bad conductors of heat and electricity. Most are based on a structure containing covalent bonds within each molecule to give them high strength in a single direction (Ferracane, 2001).

The weak nature of the interaction between each polymer chain reduces the structural and thermal stability of the materials when compared to metals and ceramics. They are used to treat the teeth and base of dentures, appliances that entirely replace the teeth and gums of an edentulous patient as temporary restorative materials for single restorations and bridges, and as adhesive agents to support the bonding between various materials and tooth structure. Their limited structural stability still restricts their use, but enhancements in fracture toughness and wear resistance have greatly expanded their applications (Ferracane, 2001).

Different types of polymers are also used as biomaterials in medicine. They are applied in a wide range varying from facial prostheses to tracheal tubes, from kidney and liver parts to heart components and from dentures to hip and knee joints as shown in Table 2.2. Moreover, polymeric materials are also used for medical adhesives and sealants and for coatings that serve a variety of functions (Davis, 2003).

Table 2.2 Examples of polymers used as biomaterials (Davis, 2003).

Application	**Polymer**
Knee, hip, shoulder joints	Ultrahigh molecular weight polyethylene
Finger joints	Silicone
Sutures	Polylactic and polyglycolic acid, nylon
Tracheal tubes	Silicone, acrylic, nylon
Heart pacemaker	Acetal, polyethylene, polyurethane
Blood vessels	Polyester, polytetrafluoroethylene, polyvinyl chloride
Gastrointestinal segments	Nylon, polyvinyl chloride, silicones
Facial prostheses	Polydimethyl siloxane, polyurethane, polyvinyl chloride
Bone cement	Polymethyl methacrylate

Polymers are employed in prosthodontics, mainly for removable prostheses, like complete or partial dentures (Figure 2.1). They are also used for denture teeth, temporary crowns, maxillofacial prostheses and impression trays. But the nature of these polymers overlaps to some extent with those used for polymer restorative, impression materials, mouth protectors, and cements (Powers and Wataha, 2008).

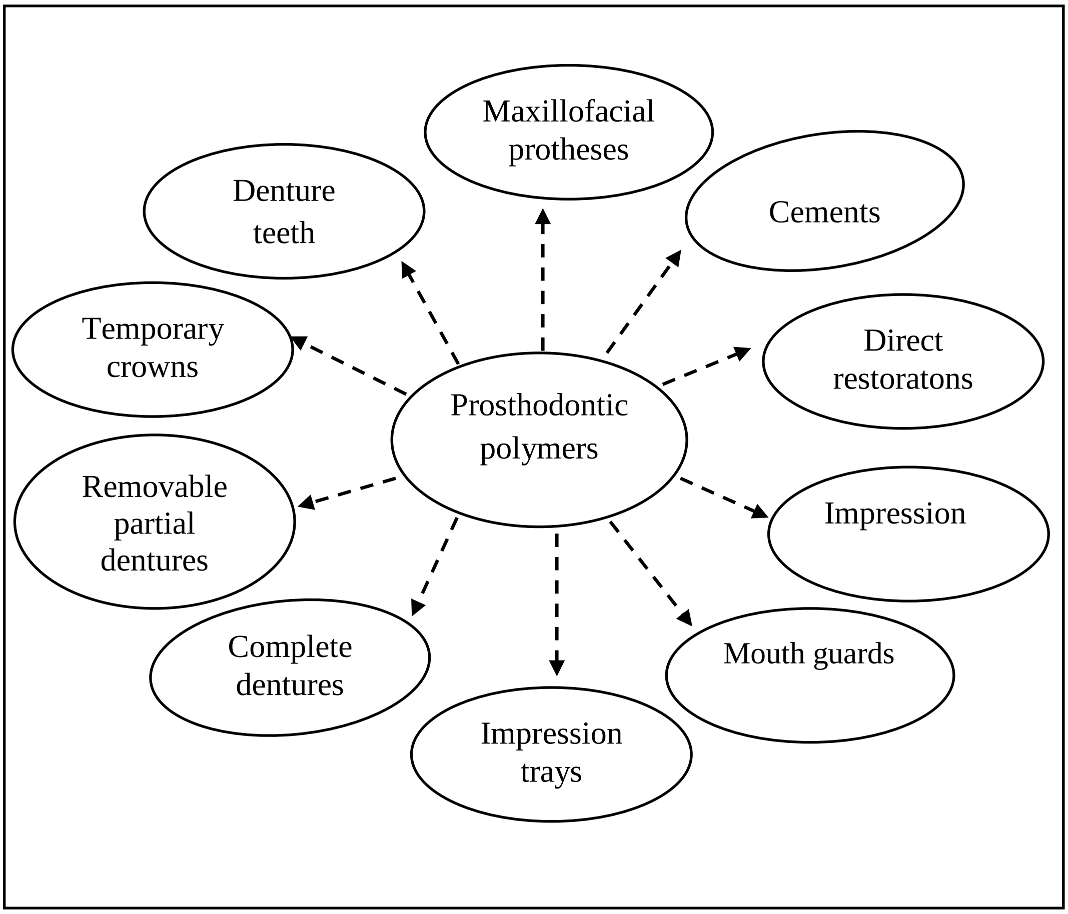

Figure 2.1 Polymers are used in a diverse array of applications in prosthodontics (Powers and Wataha, 2008).

2.3.2.1 Polymerization

The term refers to a chemical reaction that links small organic compounds called monomers into long chains of repeating monomer subunits. One polymer chain commonly contains 10,000 to 100,000 connected monomers. Due to the huge molecular weights of polymerized chains, which are greater than their monomers, the physical and chemical reaction affects the polymer. Generally, every monomer minimally keeps one chemical group that is involved in the polymerization reaction. Byproducts, such as hydrogen gas, alcohols or water are the results of the polymerization chemical reactions. These byproducts are necessary to the physical nature of the polymer (Powers and Wataha, 2008).

2.3.2.2 Cross-linked polymers

The polymer chains also contain short chains of atoms attached to their sides. The polymers are called cross-linked polymers when the side chains of adjacent polymers bond together. The polymers become easily modified, stretched or bent when side chains of adjacent polymers are joined by weak bonds. But the bond becomes stronger and the cross-linked polymers also become stronger and stiffer when adjacent polymers are joined by highly charged side chains (Hatrick et al., 2010).

2.3.2.3 Classification of polymers used in dentistry

According to Bhat and Nandish, (2007) a large number of these polymer resins, used in dentistry can be broadly classified according to:

1. Chemical repeating units.
2. Types of polymerizations.
3. Activating energies.
4. Physical states.
5. Compositions and spatial organizations.
6. Thermal behaviours.
7. Internal structure.
8. Dental applications.

2.3.3. Ceramics

Ceramics used in dentistry are nonmetallic and inorganic structures. They have compounds of oxygen with single or more metallic or semimetallic elements. Glass, porcelains, glass ceramics or highly crystalline structures are the composites of dental ceramics. For dental uses, the characteristics of ceramics are adjusted by precise control of the type and amount of the compounds used in their production. Ceramics are characterized by being better than plastics in their resistance to corrosion. But metals are much stronger than both ceramics and plastics. Despite the strong, temperature-resistant and resilient properties of ceramics, these materials are known to be breakable and may fracture when flexed or when quickly exposed to heat and cooling (Anusavice, 2003).

One of the uses of glass ceramics is as reinforcing agents or fillers, cements and temporary restorative materials. Ceramics are routinely used as coatings or veneers to enhance the esthetics of metallic dental restoration or as stand-alone veneers for anterior teeth. They are also commonly used as implant materials due to their highly biologic properties. They are sometimes used alone or as coating for metal titanium-based substances put directly into the mandible or maxilla (Ferracane, 2001). Dental ceramics could be found in dental laboratories in different types, such as liner ceramic, core ceramic, opaque dentin ceramic, enamel, stain, glaze and addition ceramic (Anusavice, 2003).

Bioceramics refers to the ceramics that have improving property for human life. They are generally used for repairing the skeletal tissues including bones, joints, teeth and hard and soft tissues. Ceramics are also involved in replacing parts of the cardiovascular system, especially heart valves (Hench and Wilson, 1993). Of the advantages of the implantable bioceramics are their nontoxic, noncarcinogenic, nonalergic, biocompatible, non inflammatory and biofunctionable nature (Wong and Bronzino, 2007).

2.3.3.1 Classification of bioceramics

Bioceramics are classified as; nonabsorbable (relatively inert)**,** biodegradable or bioresorbable (non-inert) and bioactive or surface reactive (semi-inert) (Wong and Bronzino, 2007).

(a) Bioinert ceramics

They are called so because such materials interact slightly with the surrounding tissues when they are used for human body. Examples of bioinert materials such as stainless steel, titanium, zirconia, polyethylene and alumina (Geckeler and Nishide, 2010). These materials are highly chemical stability in vivo and incorporate into the bone tissues when implanted in living bone according to the pattern "contact osteogenesis". Alumina and zirconia are highly compressive, and better biocompatible than stainless steel. Generally, the mechanical strength of bioinert ceramics is higher than that bioactive ceramics (Poitout, 2004).

(b) Bioresorable ceramics

They are known as bioresorable ceramics because when they are placed within the human body, they start to dissolve or be resorbed and gradually be replaced by natural tissues (Geckeler and Nishide, 2010). In addition, resorbable implants are intended to degrade gradually with time and be substituted with natural tissues. It leads to regeneration of tissues instead of their replacement. The rate of materials dissolution differs from one material to another. The resorbable implant is replaced normally by bone. However, during the replacement process, the thickness of the implant could result in mechanical breakdown. Therefore, the resorption rates of the material should be in line with the repair rates of body tissues (Hench and Wilson, 1993).

(c) Bioactive ceramics

Bioactive refers to a material which, upon initial placement within the human body, interacts with the adjacent bone and in some cases, even soft tissue (Geckeler and Nishide, 2010). Bioactive ceramics have the character of osteoconduction and the capability of chemical adhesion with living bone tissues. In other words, when they are implanted in living bone, they are incorporated into the bone tissue in line with the pattern of “bonding osteogenesis” (Poitout, 2004).

Bioactive ceramic mainly including calcium phosphates are demonstrating very promising results in the high bioactivity and the formation of interfacial chemical bond with host tissue. When compared with their replaced natural hard tissues, the mechanical properties of bioactive ceramics are fairly poor. The poor mechanical properties especially inside the body’s aqueous environments highly reduce their application. A number of bioactive ceramics have been proposed for hard tissue replacements; however, from the biocompatibility approach bioactive glasses and HA is the most suitable materials for hard tissue applications (Shi, 2006). According to Bader et al., (2000), ceramic materials alone do not hold the required mechanical properties to replace natural bones. Table 2.3 illustrates the mechanical properties of commercially available bioceramics.

Table 2.3 Mechanical properties of bioceramics (Bader et al., 2000)

Ceramic	Young's modulus (GPa)	Strength (MPa)	Density (gcm^{-3})	Fracture toughness ($MPa.m^{1/2}$)	Vickers hardness
Bioglass® (45S5 Glass)	35.0	(T) 42.0	2.66		458
Ceravita (Glass ceramic)	100-150	(Co) 500			
Cerabone (AW) (Glass ceramic)	118	(B) 215 (Co)1080	3.07	2.0	680
High alumina (Ceramic)	380	(B) 550 (Co) 4500	>3.93	5-6	2300
Partially stailized Zirconia	200	(Co) 1200	5.6-6.12	15	1300
Sintered HA	80-110	(B) 115-200 (Co) 500-1000	3.16	1.0	600

Note. T, tensile strength: Co, compressive: B, bending: AW, apatite wolastonite.

2.3.3.2 Applications of Bioceramics

Bioceramics are formed in a variety of types and phases and perform many dissimilar functions in healing of the body. These are summed up in Figure 2.2. Bioceramics are used, in many applications, in the form of bulk of a precise shape called implants, prostheses, or prosthetic devices. Bioceramics are also utilized to stuff space while the natural repair processes are used to restore function. Moreover, bioceramics are utilized as coating on a substrate, or a second phase in a composite, combining the features of both materials into a new material with improved mechanical and biochemical characteristics (Hench and Wilson, 1993).

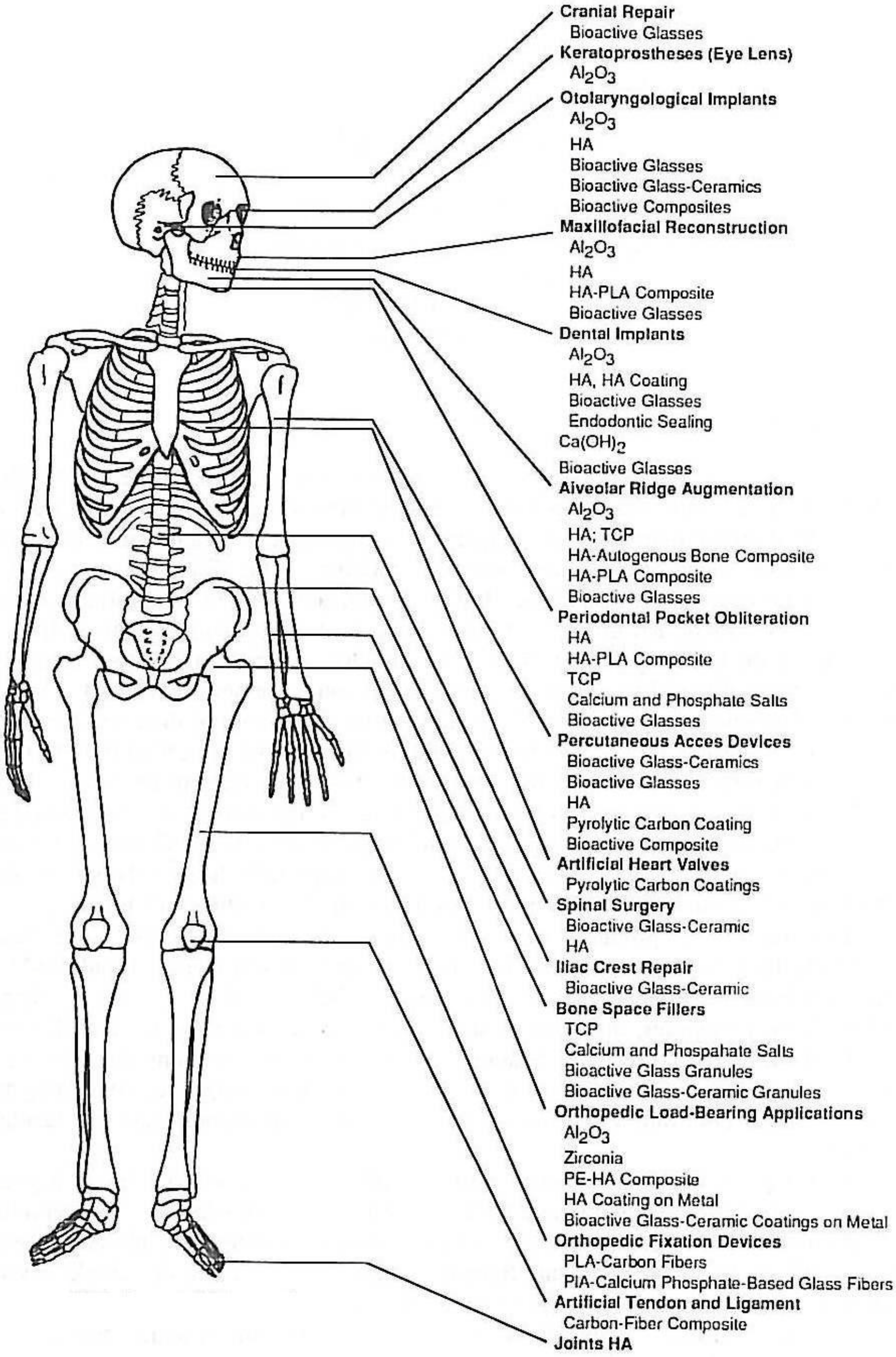

Figure 2.2 Clinical uses of bioceramics (Hench and Wilson, 1993)

2.3.3.3 Hydroxyapatite

Hydroxylapatite, also termed as hydroxyapatite (HA), is a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$. It is regularly written as $Ca_{10}(PO_4)_6(OH)_2$ to indicate that the crystal unit cell encompasses two entities. HA is the hydroxyl endmember of the complex apatite group. The OH^- ions could be substituted by fluoride, chloride or carbonate, producing fluorapatite or chlorapatite. Pure hydroxyapatite powder is white. Naturally occurring apatites could, however have brown, green, or yellow colorations, comparable to the discolorations of dental fluorosis (Wikipedia, 2010a).

HA has been effectively utilized in medicine for several years due to its outstanding biocompatibility (Hench, 1991). According to Kim et al., (2007), HA has been employed significantly in clinical applications owing to its resemblance with the mineral components of human bones and teeth. HA ceramic is frequently the material of choice for fabrication of dense and porous bioceramics employed in the reconstruction of damaged bone due to its excellent bioactivity and biocompatibility. Because it is found in natural hard tissues as mineral phase, HA is the most important among the calcium compounds. It seems to form a direct chemical bond with hard tissues. Furthermore, HA functions as strengthening in hard tissues and is accountable for the stiffness of bone, dentine, and enamel (Park and lakes, 2007).

Unfortunately, the fracture toughness (K_{IC}) of the HA ceramics does not go beyond the value of about 1 $MPa.m^{1/2}$ as compared to 2 - 12 $MPa.m^{1/2}$ for human bone. Consequently, the HA materials could not be used as heavy-loaded implants, such as artificial teeth or bones. Their medical purposes are limited to powders, small unloaded implants, coatings and low-loaded porous implants (Hench, 1991).

According to Bronzino (2000), the mineral part of bone and teeth is made of a crystalline form of calcium phosphate analogous to HA. The apatite family of mineral crystallizes into hexagonal rhombic prisms, and has unit cell dimensions a = 9.432 Å and c = 6.881 Å. The atomic structure of HA projected along the c-axis on the basal plane is shown in Figure 2.3. The hydroxyl ions are positioned on the corners of the proposed basal plane and they occur at equidistant interval (0.344 nm) along the columns perpendicular to the basal plane and parallel to the c-axis. Six of the ten calcium ions in the unit cell are connected with the hydroxyls in these perpendicular columns, ensuing strong interactions among them (Park, 2008).

HA powder is considered as an important reinforcement agent for polymers to improve their mechanical and biological properties. HA-filled organic polymers have been utilized as bone cements (Vallo et al., 1999), dental implants (Labella et al., 1994) or bone replacement material (Wang et al., 1998). Table 2.4 illustrates some properties of synthetic calcium phosphates.

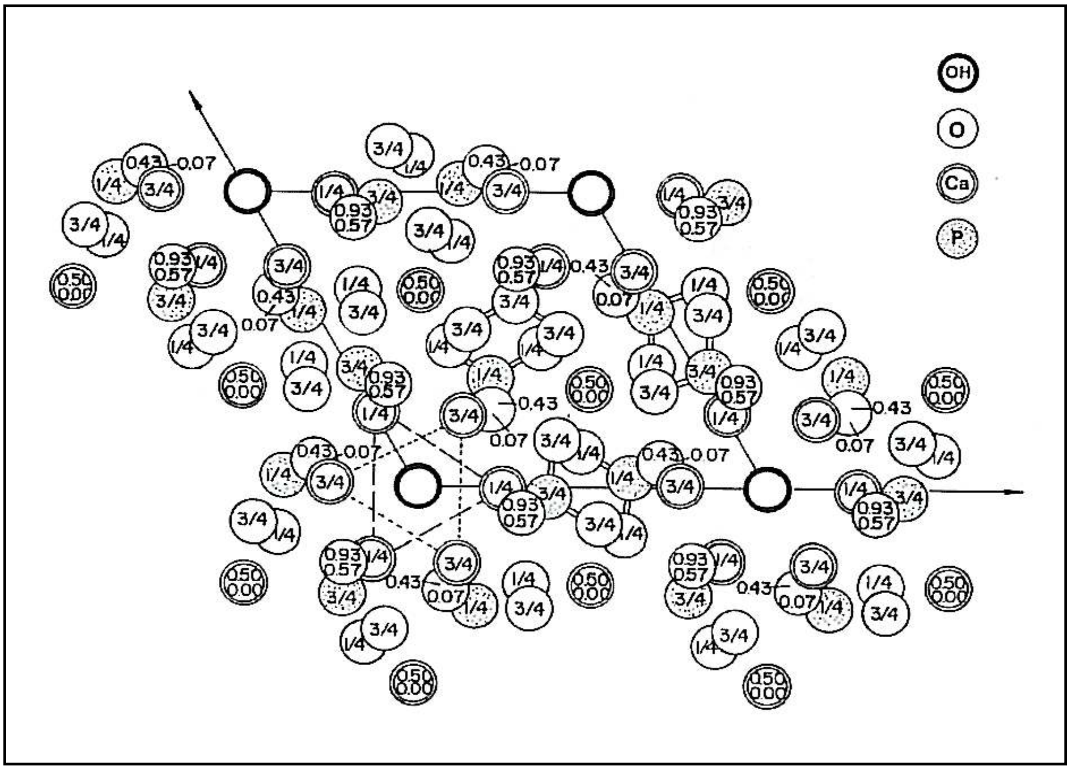

Figure 2.3 Atomic structure of hydroxyapatite (Park, 2008)

Table 2.4 Some properties of synthetic calcium phosphates (Park and lakes, 2007)

Properties	**Values**
Elastic modulus (GPa)	40 – 117
Compressive strength (MPa)	294
Bending strength (MPa)	147
Hardness Vickers	3.43
Poisson’s ratio	0.27
Theoretical density (g/cm^3)	3.16

2.3.3.4 Classification of dental ceramics

According to Bhat and Nandish (2007), dental ceramics can be classified as following:

i. According to compositions.

   Feldspathic, Leucite based, Lithia based, Aluminous, Pure Alumina, Silca and Zirconia.

ii. According to processing.

   Condensation and sintering or firing, partial sintering and glass infiltration, hot pressing, casting, slip casting, Computer Aided Designing and Computer Aided Machining, copy milling and machining.

iii. According to varieties used.

   Core porcelain, opaque porcelain, body (dentin) porcelain, gingival, neck or cervical porcelain, enamel (incisal porcelain), colour frits (pigments) and glaze porcelains.

iv. According to fusion temperatures.

   High fusing (> 1300°C) - used for artificial teeth, medium fusing (1100°C - 1300°C) - used for artificial teeth, low fusing (850°C - l100°C), crown bridges, veneers, metal ceramics, and ultra low fusing (< 850°C) - metal ceramics, casting.

v. According to microstructure.

   Amorphous glass, crystal containing glass, crystalline porcelain, and partially crystallised porcelain.

vi. According to transparency.

   Opaque, translucent and transparent.