Mechanical and environmental properties of denture base poly (METHYL METHACRYLATE) FILLED BY BARIUM TITANATE

BY

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LIST OF ABBREVIATIONS

Al	Aluminium
ASTM	American Society for Testing and Material
Ba	Barium
$BaSO_4$	Barium sulphate
$BaTiO_3$	Barium Titanate
Bis GMA	Bis-(2-Hydroxypropyl)-Methacrylate
BPO	Benzoyl Peroxide
DISMA	Diiodine salicylic methacrylate
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
EDX	Energy-Dispersive X-ray
EGDMA	Ethylene glycol dimethacrylate
h	Hour
HA	Hyroxyapatite
HDPE	High density poly ethylene
ISO	International Standardization Organization
MMA	Methyl methacrylate
MPa	Mega Pascal
MW	Molecular Weight
OD	Optical Density
PC	Polycarbonate
P/L	Powder to Liquid Ratio
PMMA	Poly (methyl methacrylate)
PSF	Polysulfone
PVP	Percutaneous vertebroplasty

SBF	Simulated body fluid
SEM	Scanning Electron Microscopy
SiO_2	Silica
Sr	Strontium
$SrTiO_3$	Strontium titanate
TA	Thermal analysis
T_g	Glass transition temperature
TGA	Thermo Gravimetric Analysis
Ti	Titanium
TIBMA	Triiodobenzoyl] ethyl methacrylate
TPB	Triphenyl bismuth
UDMA	Urethane-dimethacrylate
UHMWPE	Ultra High Molecular Weight Polyethylene
VHN	Vickers Hardness Number
Wt	Weight
ZO_2	Zirconium Oxide

LIST OF MAIN SYMBOLS

γ-MPS	3-(methacryloxy) propyl trimethoxysilane
K_{IC}	The stress intensity factor
ρ	Density
ρ_c	Density of composite
ρ_f	Density of filler
b	Specimen width
P	Load
d	Specimen thickness
L	Support span
E'	Storage modulus
V_f	Volume fraction
W_f	Weight fraction
W_0	Sample weight in air
W_1	Sample weight in water
y	Geometry correction factor

SIFAT MEKANIKAL DAN PERSEKITARAN KE ATAS ASAS DENTUR POLI (METIL METAKRILAT) TERISI BARIUM TITANAT

ABSTRAK

Tujuan kajian ini ialah untuk menyiasat penggunaan barium titanat ($BaTiO_3$) sebagai radiopasifier dalam poli (metil metakrilat) (PMMA) bagi bahan asas gigi agar memperolehi polimer yang telusradio. Formulasi yang digunakan dalam penyelidikan ini terdiri dari PMMA, $BaTiO_3$, benzol peroksida (BPO) sebagai pemula, metil metakrilat sebagai monomer dan etilena glikol dimetil akrilat (EGDMA) sebagai agen penyambung silang. $BaTiO_3$ dirawat dengan agen pengkupel silana, 3-trimetoksililpropil metakrilat (γ-MPS), sebelum ianya dimasukkan ke dalam komponen-komponen serbuk (PMMA, BPO). Rawatan permukaan ini dianalisis dengan menggunakan kaedah X-ray peleraian tenaga (EDX). Spesimen-spesimen disediakan dengan menambah komponen serbuk kepada monomer MMA disusuli dengan adunan tangan seperti yang lazim dipraktikkan dalam makmal pergigian. Empat peratusan bahan pengisi digunakan untuk digaul dengan fasa serbuk polimer dalam penyediaan sampel-sampel komposit polimer yakni 5%, 10%, 15%, and 20% berat. Acuan diisi dengan adunan/ulian tepung/doh dan dikenakan tekanan pada 14 MPa untuk 30 minit pada suhu bilik. Pematangan dijalankan menggunakan rendaman air pada suhu 78^oC selama 1.5 jam. Sampel-sampel diuji untuk ciri-ciri tensil, kelenturan dan keliatan patah. Keputusan menunjukkan bahawa pencompuran $BaTiO_3$ ke dalam matriks akan meningkatkan modulus tensil dan modulus fleksural tetapi menurunkan kekuatan tensil dan kekuatan fleksural. Peningkatan kandungan $BaTiO_3$ dalam matriks PMMA telah meningkatkan kerapuhan komposit yang terbentuk. Morfologi spesimen diperiksa menggunakan kaedah mikroskopi imbas elektron (SEM). Kesan kandungan pengisi ke atas kekerasan permukaan juga dikaji dan keputusan menunjukkan kekerasan permukaan bagi komposit PMMA telah meningkat. Ciri-ciri termal komposit PMMA dinilai dengan menggunakan kaedah imbasan kebezaan kalorimetri (DSC) dan analisis termogravimatrik (TGA) serta analisis mekanikal dinamik (DMA). Diperhatikan bahawa kehadiran pengisi yang dirawat tidak memberikan sebarang perubahan ketara dalam sifat-sifat termal komposit. Kajian penyerapan dan keterlarutan dalam air dan bendalir badan simulasi (SBF) mendedahkan bahawa sampel-sampel memperlihatkan kadar keterlarutan dan penyerapan yang rendah berbanding sampel-sampel yang tidak terisi. Kesan keadaan persekitaran terhadap kekerasan permukaan dan keliatan patah juga dikaji. Keputusan menunjukkan bahawa berlaku penurunan dalam nilai-nilai kekerasan permukaan bagi matriks PMMA dan komposit PMMA (10% jisim) sebanyak 15.5% dan 12.6% setelah direndam dalam SBF selama 28 hari. Pengurangan nilai keliatan patah pula adalah sebanyak 5.1% dan 3.5% bagi matriks PMMA dan komposit PMMA. Selain daripada itu, pengaruh pengeringan semula ke atas keliatan patah juga telah dikaji. Keputusan menunjukkan bahawa terdapat sedikit penurunan dalam keliatan patah setelah pengeringan semula iaitu 9.3% dan 10.5% bagi matriks PMMA dan komposit PMMA. Dianggap bahawa ion-ion daripada bendalir badan simulasi (SBF) akan meresap ke dalam komposit dan ion-ion tersebut pula akan dilepaskan ke medium sekelilingnya. Oleh itu, eksperimen pelepasan ion-ion ke medium sekeliling komposit dijalankan. Ion-ion atau unsur-unsur yang dilepaskan telah dilaporkan. Akhirnya, didapati bahawa radioopasiti komposit PMMA mengalami penambahbaikan apabila pengisi ditambah.

MECHANICAL AND ENVIRONMENTAL PROPERTIES OF DENTURE BASE POLY (METHYL METHACRYLATE) FILLED BY BARIUM TITANATE

ABSTRACT

The aim of the present study is to investigate the utilization of barium titanate ($BaTiO_3$) as a radiopacifier in poly (methyl methacrylate) (PMMA) for dental base material in order to obtain a radiopaque polymer. The formulation used in this study comprises of PMMA, $BaTiO_3$, benzoyl peroxide (BPO) as the initiator, methyl methacrylate as the monomer and ethylene glycol dimethyl acrylate (EGDMA) as the cross-linking agent. The $BaTiO_3$ was treated by a silane coupling agent, 3-trimethoxysilylpropyl methacrylate (γ-MPS), prior to its incorporation into the solid components (PMMA, BPO). The surface treatment was demonstrated using energy-dispersive X-ray (EDX). The specimens were prepared by adding powder to the MMA monomer followed by hand mixing as is standard dental laboratory practice. Four percentages of the filler were mixed with the polymer powder phase to prepare the 4 polymer composite samples i.e. 5, 10, 15, and 20 wt. Moulds were filled with the mixture at its dough stage and subjected to pressure at 14 MPa for 30 min at room temperature. The curing was carried out using a water bath at 78°C for 1.5 h. The samples were tested for tensile, flexural properties and fracture toughness. The results show that the incorporation of $BaTiO_3$ filler into PMMA matrix resulted in an increase tensile and flexural modulus with slightly reduction in tensile and flexural strength while fracture toughness decreased. Increases in the amount of $BaTiO_3$ incorporated to PMMA matrix, increases the brittleness of the resulting composites. The morphology of the specimens was examined using electron scanning microscopy (SEM). The influences of filler content on the surface hardness were also studied. The results showed an improvement on surface hardness of PMMA composite. The thermal properties of PMMA composite were evaluated using differential scanning calorimetry

(DSC), thermogravimatric analysis (TGA) and dynamic mechanical analysis (DMA). It was observed that the presence of treated filler did not cause any significant changes on the thermal properties of the composite. Studies on absorption and solubility in water and simulated body fluid (SBF) revealed that the filled samples showed lower solubility and absorption as compared to the unfilled samples. The effects of environmental condition on the surface hardness and the fracture toughness were also studied. The results disclosed a reduction on surface hardness of PMMA matrix and PMMA composite (10 wt%) by 15.5% and 12.6%, respectively, after 28 days of immersion. Moreover, decrease in fracture toughness values, after 28 days of immersion, was found by 5.1% and 3.5% for neat PMMA and PMMA composite, respectively. Beside this, the influence of re-drying on fracture toughness was also estimated. The results show that there was a slight decrease in fracture toughness after re-drying by 9.3% & 10.5% for the PMMA matrix and the PMMA composite, respectively. Because of the assumption that ions from the artificial saliva diffused into the composite, and then ions can leach into the surrounding medium, the leaching experiment was applied. Subsequently, the leached elements were reported. Finally, the radio-opacity of PMMA composite was enhanced when the filler percentages increased.

CHAPTER 1

INTRODUCTION

1.1 Polymers as a dental material

The use of polymer was made possible by Charles Goodyear's discovery of vulcanized rubber in 1840. Approximately twenty years after that discovery, the material was introduced as a denture base, under the brand names Ebonite and Vulcanite, to be used with porcelain teeth. These remained the principal denture base materials for 75 years despite the fact that they had poor aesthetics, tasted bad, and smelled foul. In 1868, John Hyatt discovered the first plastic molding material, celluloid, by dissolving nitrocellulose (a cotton derivative) under pressure. Celluloid was tough and somewhat flexible and had better aesthetics than vulcanized rubber, but it too tasted bad and smelled foul. It was also difficult to process and was not particularly stable. In 1909, Dr. Leo Bakeland discovered phenol-formaldehyde resins while trying to make artificial shellac. This material, which became known as Bakeland, was tried as a denture base but was found to be dimensionally unstable in the mouth. In the 1930s, Dr. Walter, Wright, and the Vernon brothers developed poly methyl methacrylate (PMMA), a hard plastic. Although other materials were used for dental prosthetics, none could come close to PMMA, and by the 1940s, 90 to 95 % of all dentures were made from this acrylic polymer (Ferracane, 2001a).

Poly (methyl methacrylate) (PMMA) is a transparent and colorless polymer. It can be made to resemble the oral soft tissue in appearance by the use of pigments. The pigments normally used are from the organic variety but unfortunately some of organic dyes have been found to be too unstable for this purpose. The most commonly used pigments are red cadmium pigments such as cadmium sulfide or cadmium sulfoselenide, which together with titanium dioxide can produce a pink denture base with realistic opacity. It has been reported that the quantity of cadmium, which is leached from denture base, is negligible compared with the normal intake from other sources. Other organic pigments are now being used which enable the denture base to match, almost exactly the oral soft tissues of the patient for whom the denture is being constructed.

PMMA currently is the material of choice for denture base fabrication. Research activity in field of denture base materials has concentrated on attempts to improve fracture toughness, impact strength and radiopacity of acrylic materials. Moreover, PMMA continues to be used because of its favorable working characteristics, processing ease, accurate fit, superior esthetics, and use with inexpensive equipment. Despite these excellent properties, there is a need for improvement in the fracture resistance of PMMA. Most fractures of the denture occur inside the mouth during service, primarily because of resin fatigue. The denture base resin is subjected to various stresses during function; these include compressive, tensile, and shear stresses. Some of the factors responsible for denture fracture include stress intensification, increased ridge resorption leading to an unsupported denture base, deep incisal notching at the labial frena, sharp changes at the contours of the denture base, deep scratches, and induced processing stresses.

Fracture toughness (K_{IC}) is an intrinsic characteristic of a material concerning resistance to crack propagation. It is a measure of the energy required to initate and propagates a crack in a material, which may lead to catastrophic failure (Bonilla *et al.*, 2003). Fractures are usually classified as brittle fracture and ductile fracture. In brittle fracture, the materials behave elastically up to the point of failure. There is hardly observable deformation of the materials prior or during breakage. The fracture surfaces are relatively smooth and largely perpendicular to the direction of the applied stress. The two surfaces can be fit together quite accurately. Ductile fracture implied that large permanent deformation has occurred before failure, requiring a significant greater amount of energy absorption by the part before failure. Since the result of permanent deformation, the fracture surfaces do not match, and the cross-sectional area at the location of the fracture is reduced from the original value.

To overcome these shortcomings, experiments with alternate polymers were conducted, but the polymers failed to produce dentures of greater accuracy or better performance. Various modifications of PMMA have also been tested to improve the existing material; these modifications include chemical modification to produce graft copolymer high-impact resins and mechanical reinforcement through the inclusion of glass fibers, nylon, or (more recently) ultra-high-modulus polyethylene fibers (John *et al*., 2001).

Denture base polymer offer an impressive range of attractive properties. However in their application they are exposed to aqueous environmental such as water and saliva in the oral cavity, which in turn affect their properties. Water sorption refers to the absorption and adsorption of water by a material. It is important to know the amount of water absorbed by denture base material, as water act as a plasticizer and effects on the mechanical properties and dimensional stability. PMMA absorb relatively small amount of water when placed in aqueous environment (Memon, 1999).

During clinical use, the denture base materials are immersed in saliva and, when not in use, may be soaked in water or cleansing agents. When immersed in such solutions, plasticizers and other soluble components may leach out over extended periods, while water or saliva is absorbed. The loss of plasticizer may cause brittleness and increased hardness values. Several investigators have evaluated the effect of water on the bond strength of acrylic materials and demonstrated that absorbed water can have a detrimental effect on bond strength to acrylic resin. Furthermore, Dootz *et al* (1993) have shown that material aging can dramatically affect the physical and mechanical properties.

The water absorption of any polymeric material whether filled or not, is of importance for dental application. Water ingress into polymers can have both detrimental and beneficial effects on the properties of the material. Water exposure also may decrease the life of resin composites by silane hydrolysis and microcrack formation. Excessive water uptake can promote breakdown causing filler-matrix debonding (Mohamed, 2006). So, it is important to know the amount of absorbed water.

The effects of simulated body fluid (SBF) and distilled water on the mechanical properties of acrylic bone cement modified with experimental oligomer filler has been determined. The results suggested that both water and SBF storage decrease the mechanical properties, however no significant differences were found between test specimens stored in distilled water or SBF. In addition the SEM examinations showed random voids in the specimens after storage in water or SBF (Puska *et al.,* 2003).

Major factors affecting thermal, physical and mechanical properties of particulate (i.e the filler) reinforced polymer composites include the polymer structure and molecular weight, the filler type and volume fraction, and the interfacial state between the filler and the polymer. Other factors such as filler surface treatment and matrix modification also play an important role. Silane coupling agents contain two different reactive groups in their molecules and one of them can be hydrolyzed. These groups allow them to forge strong connection with polymer matrix and filler particles (Wang and Bonfield, 2001). Carrodeguas et al., (2003) reported that the silanation of the $BaTiO_3$ or $SrTiO_3$ particles provides formulation with improved mechanical properties and injectability with respect to those obtained with the untreated fillers.

The effectiveness of silane coupling agent has been well established by other researchers to improve bond between inorganic filler and organic polymer matrix (Deb, 1996; Sim *et al.,* 1997; Harper *et al.,* 2000).

1.2 Problem Statement

PMMA is the most widely used denture base material. Due to the fact that it has better aesthetic value and is more stable in the mouth compared to any materials used before. In spite of that, the application of PMMA as an ideal denture base material is still restricted by a few limitation. One of them is the difficulty in achieving intrinsic radiopacity in the material. This is due to the constituent elements of PMMA. Currently, most denture plastics are radiolucent and concern exists about the difficulty of removing fragments dentures aspirated during accidents. Radiopacity is often achieved by the addition of a contrast agent, like barium sulphate ($BaSO_4$). However, the presence of this radiopacifying filler influences both the mechanical and biological behaviour of bone cements. For instance, the presence of barium sulphate reduces the tensile strength of the cement compared to radiolucent cement (van Hooy-Corstjens *et al.*, 2004) and gives insufficient levels of radiopacity (McCabe and Walls, 2002b).

During service, denture base polymer is exposed to an aqueous environment. Water is known to diffuse into the matrix polymer causing it to plasticize and weakening the mechanical properties of the composite. Water exposure also may decrease the life of resin composites by silane hydrolysis and microcrack formation. Excessive water uptake can promote breakdown causing filler-matrix debonding (Tanner *et al.,* 2001).

Generally, fracture in acrylic denture base is a common clinical problem. The fracture toughness of many dental composite resins has been previously assessed using various techniques, including the Barker "short rod" test (Smith *et al*., 1987), double torsion of rectangular bars (Goldman 1985), and bending of single-edge notch bars without pre-cracks (Lloyd and Ianetta, 1982; Lloyd, 1983; Lloyd and Mitchell, 1984). The results of these experiments have shown that more heavily filled composite resins have higher fracture toughness than do microfills, and that extended storage in water causes a reduction in fracture resistance for some materials. Examination of the fracture surfaces suggests that crack propagation is through the matrix phase (Lloyd and Mitchell, 1984).

Acrylic resin comprises chemically from C, H and O which have very low atomic number. Our approach for enhancing the properties of denture base material and their radiopaque is through the incorporation of $BaTiO_3$ filler to act as radiopacity agent due to the higher atomic number of Ba and Ti. The aim of this inclusion is to improve the ability of PMMA to absorb x-ray for achieving sufficient level of radiopacity. However, their usage in denture base radiopacifier is not widely reported in open literature.

1.3 Research Objectives

The use of particulate composites in dentistry has increased during recent years. Their mechanical properties should to be superior in applications like removable dentures. In the oral cavity, composites are exposed to an aqueous environment. Water is known to diffuse into the matrix polymer causing plasticizing of the polymer and weakening the mechanical properties of composites. On the other hand, a newly cured polymer contains residual monomers, which leach out during storage in water. These phenomena may change the mechanical and surface properties of the composite.

The objectives of this study are to produce denture base material with well balanced mechanical and environmental properties. Barium titanate, $BaTiO_3$, will be used in preparing the denture base materials. The effect of incorporation of $BaTiO_3$ on physical, morphology, mechanical and environmental properties of denture base materials is investigated. Thereby, the influences of $BaTiO_3$ on mechanical properties such as flexural, tensile strength and fracture toughness are evaluated. Moreover, its effect on thermal characterization is examined.

In this study, the effects of environmental condition on composite properties will be evaluated. The effects of $BaTiO_3$ powder in terms of solubility in a simulated body fluid environment and the absorption in both an aqueous and simulated body fluid environments is investigated. In addition, the study is also designed to estimate the effects of environmental condition on fracture toughness and hardness of composite. Subsequently, the effect of re-drying on fracture toughness is investigated. Then, the effects of $BaTiO_3$ on the radiopacity characteristics of denture base material are estimated.

1.4 Outline of Thesis Structure

Chapter one provides a brief introduction to polymers and the use of poly (methyl methacrylate) PMMA as a dental base material. Some needs for improvement in the fracture resistance of PMMA are provided with a short explanation on the effects of an aqueous environment exposure on denture base polymer properties is also stated. The objectives and the general direction of the whole research program are also carefully outlined.

Chapter two includes a definition of dentures and dental base materials as well as mention of some properties found in these materials and an enumeration of the materials used in prosthetic dentistry and types of denture base materials. This chapter outlines the kinds of polymerization before elaborating on the mixing and curing of denture base material prior to treatment of modified acrylic materials. Subsequently, a literature survey of various published works, particularly those that are closely related to this work is provided.

Chapter three describes step by step the experimental procedures employed, details of laboratory equipments used as well as processing techniques employed in generating data that were employed during the course of study.

Chapter four reports the results and discussion of this study. It commences with descriptions on the effects of filler content on the density of the composite, the determination of filler content and the presence of silane in the treated filler by using EDX. Next, it deals with the effects of barium titanate on the mechanical, thermal and morphological properties of the composite. Data, graphs and charts on the mechanical and thermal properties of the composite are presented. The chapter also studies the morphology of the fracture surface using scanning electron microscopy (SEM).

In the last part of this chapter, the environmental characteristics are discussed which include the influence of the filler on water absorption and SBF absorption and solubility. This is followed by a discussion on the effects of SBF on mechanical properties and an estimation on the effects of re-drying on both mechanical and morphological properties. Finally, the results of the effects of filler levels on the radiopacity of the PMMA composite are outlined.

Chapter five presents some concluding remarks on the present work as well as some suggestions for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Dentures

Dentures are a set of replacement teeth for any teeth that are missing. There are two types of dentures, one is known as a full denture or complete denture while the other is termed a partial denture. Complete dentures replace all the teeth on either the upper or lower part of the mouth. In contrast, partial dentures replace one to several teeth. Full dentures are held in place in the mouth by suction. In some cases, when a good suction is not possible, the use of denture creams is necessary. Partial dentures are held in place by metal clasps that wrap around some of the remaining teeth. A partial denture can also be retained in the mouth with hidden clasps, which make these dentures blend in with one’s natural dentition. The fabrication of both types of dentures is fairly similar. Both types of dentures are removable and are usually made of metal and acrylic resin that is molded to fit the exact shape of a person's tooth cavity.

Dentures afford their wearers a better quality of life. Appearance, eating, speaking, and retention of remaining teeth are all positive results obtained when a denture is worn to replace missing teeth. Appearance and smiles have much to do with how people interact with each other because much of our communication is based on either speech or facial expressions. As such, dentures definitely assist in the preservation of our abilities to communicate with one another. Finally, dentures also help to prevent tooth misalignment and tooth loss.

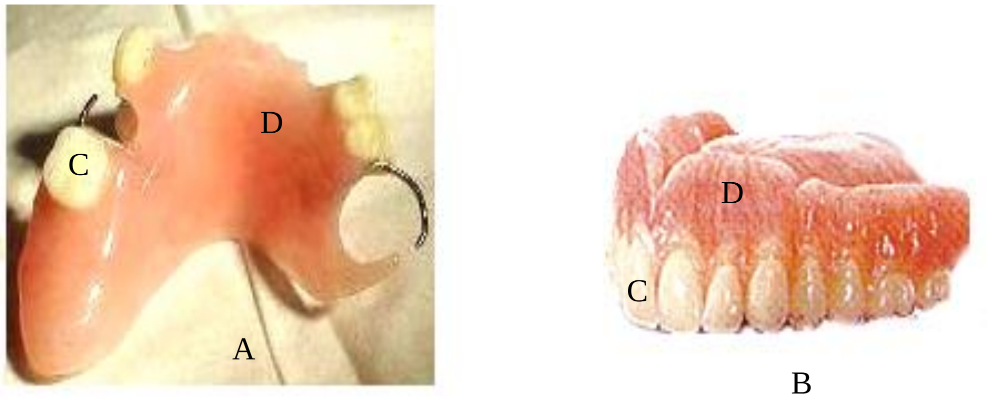

Fig. 2.1: Dentures and their compositions; (A) Partial Denture; (B) Complete Denture; (C) Artificial Teeth; (D) Denture Base Material

2.2 Definition of Denture Base Material

The denture base is that part of the denture which rests on the soft tissues of the mouth, and so does not include the artificial teeth component. Vulcanite rubber was used for a period as denture base material but it was difficult to pigment and tended to become unhygienic due to the uptake of saliva. Currently acrylic resin, poly (methyl methacrylate) (PMMA) is used almost universally for denture base fabrication (McCabe and Walls, 2002b). This fabrication is done in a two-part gypsum mould. The physical properties of the final polymer are important in the fabrication of polymeric denture base as the cured polymer should be stiff enough to hold the teeth in occlusion during mastication and to minimize uneven loading of mucus. The denture material should not creep under masticator loads if good occlusion is to be maintained. Not only does it have to have sufficient strength and resilience to withstand normal masticator forces but it must also be able to withstand sudden shock caused by impact forces. The material should not deteriorate in the aqueous environment of the mouth and should be able to withstand attacks from solvents present in food, drinks, or medications. The cured polymer has to be biologically inert and possess a low rate of foul smell formation and emission when in contact with oral flora.

During fabrication of a denture, the curing conditions and choice of materials have great influence on the denture's subsequent physical and mechanical properties. Each curing cycle or fabrication technique is a compromise that attempts to optimize the properties for a given application. For an allergy prone patient, low residual monomer content in denture base has greater priority than stiffness. For a patient requiring a soft lining, stiffness is very important if the reduced cross-sectional area of the denture is not to cause stability or loading problems (O'Brien, 1997b).

Dentists and manufactures of denture base materials have long sought for ideal materials and designs for dentures. So far, the results have been noteworthy although there are still some physical and mechanical problems with these materials.

Dentures with good aesthetic qualities that are chemically and biologically inert can be easily constructed; nevertheless, functional failure still occurs. It is difficult to find all the desired properties in a particular denture base material. Acrylic resins are popular because they meet many of the criteria outlined below:

- Natural appearance
- Ease of manipulation
- High flexural strength, hardness and toughness/durability
- Low density
- Dimensional stability and accurate reproduction of surface detail
- Absence of odour, taste or toxic products
- Resistance to bacterial growth
- Resistance to absorption of oral fluids
- Ease of repair
- Ease of cleaning
- Good shelf life and low cost of material

Memon, (1999) states that dentures made from acrylic resins are easy to process using inexpensive techniques and are esthetically pleasing.

2.3 Materials Used in Prosthetic Dentistry

Dentures are commonly made of metal or resin. Metal has isotropic strength, which allows the production of thin palatal plates for dentures. In contrast, resins have good esthetic properties and do not cause the allergic reactions often associated with metals. The selection of metal or resin is often determined according to purpose. In addition to these two elements, polymethacrylate, urethanedimethacrylate, polycarbonate, and polysulfone are used as base polymers in dentures (Kanie *et al.,* 2004).

2.3.1 Metals:

Metals are materials composed of metallic elements that possess the characteristics of high thermal and electrical conductivity, ductility, opacity, and luster. They also have relativity high strength and generally melt at high temperatures. Most metals are not pure but are a combination of two or more metallic elements. Alloys are formed when the atoms from one metal is dissolved within the atoms and crystals of a second metal. This process of combining metals is called alloying, and the resultant metal produced is known as an alloy. There are many different types of alloys; some are complicated while others are relatively simple in structure.

The criteria of metals and alloys in used in dentistry are specific. They must be strong enough and hard enough to withstand wear and occlusive forces. Moreover, they must be biologically compatible. They must also have a high resistance to corrosion, and they must be relatively easy to cast into complicated shapes and structures utilizing techniques that are not cost prohibitive. The metal alloys that best satisfy these requirements are the precious metals. They are termed “noble” because they are resistant to corrosion and tarnish. Gold, palladium, and platinum are the most common precious metals used in dental alloys (Ferracane, 2001c).

Alloys based on cobalt or nickel and containing a substantial amount of chromium are suitable for the construction of removable partial denture frameworks, full denture bases, and temporary tooth borne surgical and periodontal splints (McCabe and Walls, 2002c). Most recently, titanium and titanium alloys have been developed as dental casting alloys. These metals are used with porcelain. Titanium is very reactive to oxygen and has a very high melting point. Therefore, special casting equipment is required in the production of dental prostheses from titanium. Although titanium has excellent biocompatibility, the extra effort and cost required to cast this metal has limited its use as a dental restorative (Ferracane, 2001c).

2.3.2 Ceramics:

Ceramics possess such characteristics as high melting point, low thermal and electrical conductivity, high compressive strength and stiffness, low tensile strength, brittleness, and optical qualities varying from clear to translucent to opaque. They are also relativity inert and insoluble. Ceramics, predominantly porcelains, have been used in dentistry for at least 200 years. One of their first uses was in the production of dentures, a purpose for which they are still used today.

Ceramics can be defined as a class of materials composed of metallic oxide compounds. Therefore, all ceramics have similar compositions. In any case, the main building block of ceramics is the silicon dioxide molecule (silica or SiO_2). Dental ceramics and porcelain are composed of quartz or flint (silica), feldspar (a potassium-aluminum silicate), and kaolin clay (aluminum silicate). Another important component of porcelain is leucite. Leucite is a crystalline potassium-aluminum-silica mineral that forms when feldspar and glass are melted together within the porcelain. Leucite is often added as a component because it strengthens, toughens, and raises the thermal expansion coefficient of normal feldspar porcelain. In addition to this glass modifier, pigments (metallic oxides) are added to porcelain for color.

Three types of porcelains are commonly used in dentistry. One particular type is used to make denture teeth. This porcelain is called “high fusing” because it fuses at approximately 1300 to 13500ºC. A second type of porcelain is known as low-fusing porcelain and has a fusion range of 850 to 1050ºC and is used as a veneer for metal in PFM restorations. A medium-fusing porcelain (fusing point of 1100 to 1250ºC) is used for the anterior porcelain jacket crown and has properties intermediate between those of the low- and high-fusing porcelain types (Ferracane, 2001c).

The application of porcelain teeth to the denture base is recommended rather than the application of acrylic teeth due to the high resistance of porcelain teeth to abrasion, fatigue, and mastication forces during function. However, the use of porcelain teeth may cause crazing of the base in the region around tooth neck due to differences in the coefficient of thermal expansion between porcelain and acrylic resin. Applications of ceramic materials with denture base will allow for the creation of a good interface and enhanced homogeneity between the porcelain teeth and the denture base.

2.3.3 Composites:

Composites are produced when two or more materials or phases are used together to give a combination of properties that cannot be attained otherwise. Composite materials may be selected to give unusual combination of stiffness, strength, high-temperature performance, corrosion resistance, hardness, or conductivity. Composites highlight how different materials can work in synergy. Wood, bone, and teeth are examples of naturally occurring composites

In composites, the properties and volume fraction of individual phases are important. Usually the matrix phase is the continuous phase and the other phase is said to be the dispersed phase. Composites are often classified based on the shape or nature of the dispersed phase e.g., particle-reinforced, whisker-reinforced, or fiber-reinforced composites. (Askeland and Phulé, 2003).

Fillers are differentiated by certain characteristics such as particle size and distribution, geometry and surface area. Harper (2000) describes that particles of smaller size achieve better properties enhancement compared to particles of larger dimensions.

Composite resins are resins that contain a combination of hard, inorganic filler particles bonded to polymer. As a consequence of the bonded filler phase, these materials have much better mechanical properties than did unfilled resins. Composite resins for dental use were formulated to combine the needs for esthetics and ease of use of polymerizable resin base with the improved properties to be gained from the addition of ceramic filler.

The organic polymer matrix in presently available composites is most commonly an aromatic or urethane diacrylate oligomer such as bisphenol A-glycidyl methacrylate (Bis-GMA) or urethane-dimethacrylate (UDMA). Fillers are necessary for various reasons, such as improving strength, handling properties and radiopacity. Radiopacity may be conferred by incorporating elements of high atomic number, such as barium, strontium, and zirconium (O'Brien, 1997c).

2.3.4 Polymers:

Polymers are extended chain molecules, consisting of many repeating units. A monomer is the smallest repeating unit in the polymer chain. A polymer or polymer intermediate with relatively few structural units is called an oligomer. Polymers are commonly used as dental restoratives, prosthodontics and impression materials (Combe *et al.*, 1999).

The polymer beads are transparent. Some are covered with pigment to match the color of the oral tissue or tooth structure. As light penetrates the polymerized resin, the pigment reflects the light to produce a pink hue. At the same time, the resin exhibits a translucence that matches that of the human tooth or soft tissue to the extent that is opaque (Phillips *et al*, 1999).

Polymers have a major role in most areas of dentistry. Their distinctive properties allow a range of clinical applications not possible with other type of materials. However, the primary use of polymers in terms of quantity is in the construction of complete dentures and the tissue-bearing portions of partial dentures (McCabe and Walls, 2002b).

2.4 Types of Denture Base Polymers

The most common denture base polymer is dental acrylic, or PMMA. This dental resin has essentially the same composition as commercial Plexiglas but is pigmented and processed differently. The conventional versions are cured or hardened by the application of heat. Other similar formulations are cured by self curing reactions or by the application of microwave energy.

2.4.1 Acrylic denture base materials

Table 2.1: Classification of denture base polymers according to ISO 1567.

Types	Class	Description
1	1	Heat-processing polymers, powder and liquid
1	2	Heat-processed (plastic cake)
2	1	Auto-polymerized polymers, powder and liquid
2	1	Auto-polymerized polymers,(powder and liquid pour type resins)
3	-	Thermoplastic blank or powder
4	-	Light-activated materials
5	-	Microwave-cured materials

Acrylic resin is the most widely used material for the construction of dentures. Polymeric denture base materials are classified into five groups (or types), as shown in Table 2.1. Types 1 and 2 are the most widely used products and are further elaborated above.

2.4.1.1. Composition of type 1 and type 2 materials

Most materials are supplied as powder and liquid, details of the composition of which are given in Table 2.2. The major component of the powder is beads of poly (methyl methacrylate) with diameters up to 100 µm. These are produced by a process of suspension polymerization in which the methyl methacrylate monomer, containing an initiator, is suspended as droplet in water. Starch or carboxymethylcellose can be used as thickeners and suspension stabilizers to the droplet but have the disadvantage of potentially contaminating the polymer beads. The temperature is raised in order to decompose the peroxide and bring about polymerization of the methyl methacrylate to form beads of poly (methyl methacrylate) which, after drying, form a free flowing powder at room temperature.

Table 2.2: Composition of acrylic denture base materials (McCabe and Walls, 2002).

Powder	Polymer	poly (methyl methacrylate) beads
	Initiator	A peroxide such as benzoyl peroxide (approximately 0.5 %)
	Pigments	Salts of cadmium or iron or organic dyes
Liquid	Monomer	Methyl methacrylate
	Cross-linking agent	Ethyleneglycoldimethacrylate (approximately 10 %)
	Inhibitor	Hydroquinone (trace)
	*Activator	*N N'*-dimetheyl-*p*-toluidine (approximately 1 %)

* *Only in self-curing materials.*

The initiator, present in the powder, may consist of unreacted peroxide remaining after the production of beads plus additional peroxide added to the beads after their manufacture.

Poly (methyl methacrylate) is a clear, glass-like polymer and is occasionally used in this form for denture base construction. It is more normal, however, for manufacturers to incorporate pigments and opacifiers in order to produce a more lifelike denture base. Sometimes, small fibers coated with pigment are used to give a veined appearance. The pink pigments used in denture base resins are traditionally salts of cadmium. These pigments have good color stability but cadmium can leach out from the denture base in minute amounts. Fears over the toxicity of these cadmium compounds, however, have led to the gradual replacement of cadmium salts with other safer substances.

The major component of the liquid is a methyl metacrylate (MMA) monomer. This is a clear, colorless, low viscosity liquid with a boiling point of 100.3°C with a distinct odour which is exaggerated by relatively high vapour pressure at room temperature. This liquid normally contains some crass-linking agent. MMA is one of a group of monomers which are very susceptible to free radical addition polymerization. The substance most widely used in this process is ethylene glycol dimethacrylate. This compound is used to improve the physical properties of the set material.

An inhibitor, Hydroquinone, is used to prolong the shelf life of the liquid component. In the absence of this inhibitor, polymerization of monomer and cross-linking agent would occur slowly, even at room temperature and below, due to the random occurrence of free radicals within the liquid. The source of these free radicals is uncertain, but once formed they cause a slow increase in viscosity of the liquid and may eventually cause the liquid component to solidify.

The inhibitor works by reacting rapidly with radicals formed within the liquid to form stabilized radicals which are not capable of initiating polymerization. One way of reducing the occurrence of unwanted radicals in the liquid is to store the material in a can or in a dark-brown bottle as visible light or ultra-violet radiation may activate compounds which are potentially capable of forming radicals.

The activator is present only in those products which are described as self-curing or auto-polymerizing materials and not in heat curing denture base materials. The function of the activator is to react with the peroxide in the powder to create free radicals which can initiate polymerization of the monomer (McCabe and Walls, 2002).

2.4.2 Conventional heat-cured poly (methyl methacrylate)

Conventional heat-cured PMMA is supplied in the form of a powder and liquid. The powder supplied is of a very high molecular weight. It contains a copolymer of PMMA in the form of spheres or beads to which the benzoyl peroxide initiator is added. Coloring pigments and fibers are also often added to improve esthetics. On the other hand, the liquid consist of a methyl methacrylate (MMA) monomer with a cross linking agent (usually 5 to 15% ethylene glycol dimethacrylate) and a small amount of inhibitor (hydroquinone) to avoid premature polymerization and to enhance shelf life. The cross-linking molecules are added to reduce the likelihood that small surface cracks will form in the denture when it is allowed to dry. These small cracks are called craze cracks and are produced by stresses created during the drying.

MMA is an inflammable liquid of low viscosity, like water. It is volatile and boils at approximately 100°C. When it polymerizes, it shrinks approximately 21 % by volume. It can be physical irritant to the skin, producing an itchy feeling, and is a known allergen. A correctly heat-processed denture base could have as little as 0.3 % to as much as 2% residual monomer. The low temperature at which conventional dentures are processed ensures thorough, although not complete, polymerization. In contrast, high-temperature processing also leads to greater dimensional change but results in shrinkage of approximately 0.4% across the molar region (Ferracane, 2001b).

Kawara *et al*. (1998) verified that the shrinkage of heat activated acrylic denture base resin is caused mainly by thermal contraction after processing. Furthermore, they examined the degree of distortion resulting from long, low-temperature processing and compared the results with that of the conventional method. The results revealed quantitatively that the shrinkage of heat activated acrylic denture base resin was mainly thermal shrinkage. This implied that the low-temperature method was more advantageous in reducing thermal shrinkage.

Schneider *et al*. (2002) compared the tensile bond strengths of heat- and microwave-polymerized acrylic resins among 4 types of acrylic resin denture teeth. The results suggested that the type of denture base material and denture tooth selected for use may influence the tensile bond strength between the tooth and its base. Thus, it can be deduced that the selection of more compatible combinations of base and resin teeth may reduce the number of prosthesis fractures and resultant repairs. Overall, higher bond strengths were obtained with the conventional heat-polymerized acrylic resin rather than the microwave-polymerized acrylic resin.

2.4.3 High-impact acrylic

High-impact acrylic denture base is also made by the heat-cured dough method; impact resistance arises from the incorporation of a rubber phase into the beads during their polymerization. Certain rubber will dissolve in methyl methacrylate monomers, notably in copolymers of butadiene with styrene and/or methyl methacrylate. The rubber remains soluble in the monomer globule until the polymer content of the globule becomes too high and the rubber begins to precipitate out. The nature of this precipitation is complicated by the fact that some of the growing chains of PMMA may have become grafted to the butadiene rubber. The monomer used to obtain high-impact beads differs from conventional monomers in that it contains either very little or no cross-linking agent (O'Brien, 1997b).

2.4.4 Cold-cured poly (methyl methacrylate)

Cold-cured, or self-curing, PMMA often is referred to as “pour risen” because it is poured into a processing mold made of agar hydrocolloid to form a denture base. The composition of this material is the same as the heat-cured version, with two differences i.e. the powder contains beads of polymer that have a lower molecular weight than those of the heat-cured material; and the liquid contains a chemical activator (an amine molecular) to start the reaction. Denture bases made from these resins are processed quickly at room temperature. They have more residual monomer (1 to 4%) but lower dimensional change (0.2%) than denture produced by heat processing (Ferracane, 2001b).

The pour technique for dentures, originally developed during the 1960s, has lost much of its popularity because of problems that stem from incorrect processing. In this technique, the acrylic is mixed to a liquid consistency, and then poured into a sprued mold that consists largely of reversible hydrocolloids. The fitting surface of the mold consists of the plaster moldel itself; the acrylic teeth occupy their positions in the agar mold in the same way they do in a conventional plaster mold.

The poured-type mold itself has design weaknesses. The gelatinous agar cannot grip the teeth as easily as does the rock-hard plaster mold. Hence, there is a greater tendency for the teeth to be displaced during acrylic pouring. Secondly, prior to being placed in the mold, the teeth themselves have been part of the wax-up. Thus, any wax remaining on the teeth will prevent the monomer from the wetting their surfaces. This problem is far less common when solution and diffusion of the wax can occur at the elevated temperature of the heat-curing process.

The use of a hydroflask to generate increased atmospheric pressure around the mold has two main advantages. Firstly, porosity caused by monomer boiling is prevented by simply raising its boiling point. Furthermore, air included during mixing is compressed and this raises the density of the cured resin and improves its transverse strength. Due to these improvements, the creep of these products is greater than that of heat-cured acrylics.

However, the technician can do little to reduce free-monomer content to achieve high toughness, because this aspect is built into the formulation when the manufacturer selects the powder/liquid ratio, the cross-linker content, and the accelerator/catalyst ratio (O'Brien, 1997b).

2.4.5 Injection-molded polymers

Injection-molded polymers are usually made of nylon or polycarbonate. The material is supplied as a gel in the form of a patty that must be heated and injected into a mold. The equipment for processing these polymers is more expensive than that for processing conventional denture resins. In addition, the craze resistance of these materials is not equivalent to that conventional acrylic. Nevertheless, these polymers have high impact resistance and do not contain MMA monomer. As such, they may be used for patients who are allergic to MMA (Ferracane, 2001b).

2.4.5.1 Acrylic

Acrylic is supplied as granules of low-molecular-weight (MW=150.000) linear PMMA, with a narrow molecular weight range and only a small amount of residual free-monomers. There is no cross-linking, as this would increase the melt viscosity during molding. Besides this, despite the molecular weight, plasticization is low and often results in stiffness which is slightly in excess to that of conventional heat cured denture base.

2.4.5.2 Polycarbonate

This tough plastic is supplied as granules but is not suited to injection into damp molds. This is because it has a high melt viscosity and may depolymerize explosively if overheated in the presence of water. Furthermore, the absence of cross-linking results in poor solvent resistance and craze resistance. Finally, the high melt viscosity exacerbates problems of tooth attachment.

2.4.5.3 Nylon or polyamides

The first dental use of nylon was not a success due to excessive water absorption of the type chosen, which resulted in excessive creep and some biodegradation. More recent work on glass-reinforced nylons with much lower water absorption capacity has produced more encouraging results. The glass increases the stiffness of the nylon to about that of a conventional heat-cured denture base from a stiffness of half when only glass-bead reinforcement is used. Glass-fiber reinforcement should be used with care, and patients should be warned not to abrade the fitting surface so as to avoid exposing irritation-causing fibers (O'Brien, 1997b).

Phoenix, (1997) evaluated the injection moulding system in combination with microwave polymerization vis-à-vis the conventional compression technique. He reported that the injection-moulding process has an advantage over the conventional compression moulding from a health and safety perspective in terms of eliminating the direct handling of the material. From the laboratory perspective, injection-moulding processing could be completed in a relatively short time and under or over-packing of the mould cavity could be reduced. Nevertheless, some disadvantages like additional cost of the system and the necessity of adding and removing sprues were reported.