

**EFFECTS OF COUPLING AGENTS ON THE
PROPERTIES OF POLY(METHYL
METHACRYLATE)/HYDROXYAPATITE
COMPOSITES FOR DENTURE BASE
APPLICATION**

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UNIVERSITI SAINS MALAYSIA

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**EFFECTS OF COUPLING AGENTS ON THE PROPERTIES OF
POLY(METHYL METHACRYLATE)/HYDROXYAPATITE
COMPOSITES FOR DENTURE BASE APPLICATION**

by

THAM WEI LING

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- A.4 Paper 2 Journal of Applied Polymer Science (Published)
- A.5 Paper 3 Express Polymer Letters (Published)
- A.6 Paper 4 Journal of Composite Materials (Accepted)
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LIST OF ABBREVIATIONS

Al	Aluminum
ASTM	American Society for Testing and Materials
Ba	Barium
BaSO ₄	Barium sulphate
BBC	Bioactive bone cements
BET	Specific surface area
BPO	Benzoyl peroxide
C	Carbon
Ca	Calcium
Ca/P	Calcium/Phosphorus ratios
CaCO ₃	Calcium carbonate
DMTA	Dynamic mechanical thermal analysis
EDX	Energy Dispersive X-ray
EGDMA	Ethylene glycol dimethacrylate
FESEM	Field Emission Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
H	Hydrogen
HA	Hydroxyapatite
HDPE	High density poly(ethylene)
HEMA	2-hydroxy ethyl methacrylate
HIPS	High impact polystyrene
ISO	International Organization for Standardization
K	Potassium
KR TTS	Isopropyl triisostearoyl titanate

LEFM	Linear elastic fracture mechanics
MAA	Methacrylic acid
MMA	Methyl methacrylate
γ -MPS	3-methacryloxypropyltrimethoxysilane
N	Nitrogen
Na	Sodium
O	Oxygen
P	Phosphorus
PA	Polyamide
PEEK	Polyetheretherketone
PHBHV	Polymer-poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PP	Poly(propylene)
SBF	Simulated body fluid
SEN-B	Single edge notch bending
Si	Silicon
SiO ₂	Silica
Sr	Strontium
TCP	Tricalcium phosphate
TEGDMA	Triethylene glycol dimethacrylate
Ti	Titanium
TRMC	Thermoplastic resin matrix composite
XRD	X-Ray Diffraction
Zr	Zirconium

LIST OF SYMBOLS

f	Amount of filler
X	Amount of silane
D	Diffusion coefficient
T_g	Glass transition temperature
P	Load
E''	Loss modulus
a	Notch length
ppm	Part per million
M_t	Percentage change at time, t
M_m	Percentage of maximum moisture absorption
rpm	Revolutions per minute
E'	Storage modulus
K_{IC}	Stress intensity factor
w	Surface area coverage per gram
A	Surface area of the filler
$\tan \delta$	Tangent delta
m	Tangent gradient of the initial straight line
θ	Theta
W_w	Weight of specimen after exposure to water
W_d	Weight of specimen prior exposure to water

KESAN-KESAN AGEN PENGKUPEL ATAS SIFAT-SIFAT KOMPOSIT POLI(METIL METAKRILAT)/HIDROKSIAPATIT BAGI KEGUNAAN GUSI PERGIGIAN

ABSTRAK

Komposit poli(metil metakrilat) (PMMA) yang mengandung 5 wt% hidroksiapatit (HA) disediakan dengan kaedah pempolimeran haba serbuk polimer dan cecair. Dalam fasa 1, PMMA dan HA serbuk dikisarkan dengan pengisaran bebola planet. Kesan masa pengisaran dan saiz partikel bagi serbuk PMMA/HA terhadap sifat-sifat pelenturan dan morfologi bagi komposit tersebut telah diselidik. Masa pengisaran yang sesuai ialah 90 min. Bagi serbuk PMMA/HA yang disediakan dengan pengisaran bebola planet, modulus pelenturan bagi komposit PMMA telah dipertingkatkan. Pengisaran bebola planet berkeupayaan untuk meningkatkan luas permukaan partikel halus dalam komposit. Hal ini menghasilkan pertaburan HA yang lebih seragam, dan mengurangkan kandungan lompong dalam matrik PMMA. Pengurangan kandungan lompong boleh diperhatikan di atas permukaan patah komposit PMMA melalui ujian mikroskop penskanan elektron pemancaran medan (FESEM). Dalam fasa 2, permukaan HA dirawat dengan tiga jenis agen pengkupel, iaitu agen pengkupel silana, titania dan zirconia. Kandungan agen pengkupel adalah berdasarkan 2, 4, 6, dan 8% terhadap HA. Perawatan kimia bagi HA tersebut telah diuji dengan spektroskopi inframerah terjelma fourier (FTIR). Sifat-sifat mekanikal bagi komposit PMMA/5HA telah dicari dengan ujian kekuatan tensil, kekuatan pelenturan dan keliatan rekahan. Penambahbaikan sifat-sifat mekanikal adalah berhubungkait dengan peningkatan interaksi antaramuka PMMA dan HA yang disebabkan perawatan agen pengkupel. Hal ini dapat diperhatikan melalui FESEM dan sinaran-X tenaga penyerakan (EDX). Sifat-sifat termal bagi komposit PMMA/5HA telah dikaji dengan analisis termal mekanikal dinamik (DMTA), kalorimetri penskanan pembezaan (DSC) dan analisis termogravimetrik (TGA). Peningkatan sifat-sifat termal bagi komposit PMMA/5HA telah dipertingkatkan dengan perawatan γ -MPS. Dalam fasa 3, kinetik penyerapan air dan bendalir badan disimulasikan (SBF) serta kesannya terhadap sifat pelenturan bagi komposit PMMA/HA selama dua bulan perendaman telah dikaji. Kaedah matematik yang digunakan untuk menganalisis data ini ialah model peresapan fasa tunggal bebas, yang beranggapan peresapan Fickian, dengan menggunakan hukum resapan Fickian kedua. Kinetik penyerapan air dan SBF bagi komposit PMMA/HA didapati mengikut kelakuan hukum Fickian, yang mana penyerapan lembapan awal adalah mengikut perhubungan lurus dengan kenaikan peratusan berat dalam masa t dan $t^{1/2}$, diikuti dengan ketepuan. Bagi ujian sinaran-X, adalah didapati bahawa kelakuan radiopasiti bagi komposit PMMA/HA telah ditambahbaik dengan perawatan agen pengkupel. Secara keseluruhannya, komposit PMMA/HA yang dirawat dengan 8% γ -MPS dapat mencapai keseimbangan dari segi sifat-sifat mekanikal, termal, kerintangan air dan kelegapan radio dalam kegunaan gusi pergigian.

EFFECTS OF COUPLING AGENTS ON THE PROPERTIES OF POLY(METHYL METHACRYLATE)/ HYDROXYAPATITE COMPOSITES FOR DENTURE BASE APPLICATION

ABSTRACT

Poly(methyl methacrylate) (PMMA) composites containing 5 wt% hydroxyapatite (HA) was prepared by using heat-processing polymers powder and liquid method. In phase 1, both PMMA and HA powder were grounded using planetary ball milling. The effects of the grinding time and particle size of the PMMA/HA powder on the flexural properties and morphology of the composites was investigated. The suitable grinding time is 90 min. For the planetary ball mill-ground PMMA/HA powder, the flexural modulus of the respective PMMA composites was slightly increased. Planetary milling is capable of increasing the surface area of fine particles in the composites specimens, which resulted in a more homogeneous distribution of HA and a reduction of void contents in PMMA matrix. This phenomenon was evidenced by field emission scanning electron microscopy (FESEM). In phase 2, HA was surface treated with three types of coupling agent, i.e., silane coupling agent, titanate coupling agent and zirconate coupling agent with different concentrations based on HA (2, 4, 6, and 8%). The chemical treatment of HA was examined using fourier transform infrared spectroscopy (FTIR). The mechanical properties of PMMA/5HA composites were characterized using tensile, 3-point bending flexural and fracture toughness tests. The improvement of the mechanical properties could be related to the enhancement of interfacial interaction between PMMA and HA by the surface treatment of coupling agents which can be evidenced by FESEM and energy dispersive X-ray (EDX). The thermal properties of PMMA/5HA composites were evaluated using dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). The thermal properties of PMMA/HA composite was increased significantly by the γ -MPS treatment. In phase 3, the kinetics of water absorption and simulated body fluid (SBF) absorption and their effects on the flexural properties for PMMA/HA composites was studied for an immersion period of 2 months. The mathematical treatment used in analyzing the data was the single free phase model of diffusion, which assumed Fickian diffusion and utilized Fick's second law of diffusion. The kinetics of water absorption and SBF absorption of the PMMA/HA composites conformed to Fickian law behavior, whereby the initial moisture absorption follows a linear relationship between the percentage weight gain at any time t and $t^{1/2}$, followed by saturation. For X-ray evaluation test, it was found that the radiopacity behaviour of the PMMA/HA was improved by the coupling agent treatment. In overall, PMMA/HA composite treated with γ -MPS can achieved a balance of properties in term of mechanical, thermal, water barrier and radiopacity behavior in which make it suitable for denture base application.

CHAPTER 1

INTRODUCTION

1.1 Polymeric denture base materials

The ideal denture base material should possess several key physical attributes include biocompatibility, good esthetic, high bond strength with available denture teeth, radiopacity, ease of repair and greater in physical and mechanical properties. The denture base must be strong enough to allow the prosthesis to withstand functional and parafunctional masticatory forces. Poly(methyl methacrylate), urethanedimethacrylate, polycarbonate and polysulfone are used as base polymers in dentures. However, the properties of polymers resins are not as good as metals. Therefore, this is important to enhance the strength of denture base resins to incorporate some type of reinforcement into the denture base (Kanie et al., 2004).

The high incident of damage and repair to dentures are caused by tooth-to-denture base separation. Therefore, it appears that the bond between resin denture teeth and the denture base has remained unreliable, inconsistent and unpredictable. Since then, the best bonds were reported that the denture base acrylic was processed to methyl methacrylate (MMA) teeth by use of compression molding and slow heat polymerization (Zuckerman, 2003). Nowadays, resin-based materials are widely used in restorative dentistry. The most common denture base polymer is dental acrylic or PMMA. PMMA remains the preferred material for removable complete and partial prosthesis. Besides, PMMA materials are based on its low cost, relative ease of use, stability in the oral environment, aesthetics and reliance on simple processing equipment resulted in its extensive use as a denture base polymer (Narva et al., 2005a; Meng & Latta, 2005). It also has the potential to elicit irritation, inflammation

and allergic reaction in the oral mucosa (Ozen et al., 2006). However, there is significantly a difference in the chemistry among denture base based on PMMA. PMMA rely on high levels of crosslink resin and heat activated initiators to maximize the physical properties (Meng & Latta, 2005). When PMMA used as a denture base material, the powder-like polymerized PMMA beads are mixed with liquid monomers methacrylate consists of a small percentage of dimethacrylate crosslinker (Vuorinen et al., 2008). Cross-linking agents are added to PMMA to produce stronger and more fracture-resistant denture base materials. However, the mechanical strength of poly(methyl methacrylate) (PMMA) based denture base materials remains far from ideal for maintaining the longevity of dentures (Seo et al., 2006).

Denture fracture due to flexural fatigue is a common problem of clinical use. The denture base resin is subjected to various stresses during function of compressive, tensile and shear stresses. These 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 (John et al., 2001). Factor that contribute to stress concentration and increase flexing are able to induce the initiation and propagation of crack, thereby influencing the strength of dentures. The majority of denture fractures occur by the end of three years in service and fracture may occur slowly during function of masticatory force. Methods to improve the inherent material properties of PMMA include the use of alternate polymer such as polycarbonate, nylon, co-polymer and reinforcing agents including particulates and fibers (Franklin et al., 2005). The degradation of denture polymers resulting in cyclic mechanical loading and thermal stress has been reported. The

decrease of mechanical properties of denture base materials is due to a higher residual monomer content in the autopolymerizing reline acrylic resins relative to the heat-polymerized acrylic resin used as denture base materials. Moreover, the distribution of stress within a specimen can be affected by specimen shape and dimension (Seo et al., 2006).

1.2 PMMA composite denture base

Mechanical properties of PMMA based denture base materials are often insufficient for clinical use (Vuorinen et al., 2008). Acrylic based resin is of insufficient strength and may fracture through uneven masticatory force or accidental damage (Chen et al., 2001). Preiffer et al. (2005) reported that flexural failure of denture base materials is considered the primary mode of clinical failure. Consequently, several types of reinforcement materials such as glass fiber (Kanie et al., 2004; John et al., 2001), glass flake (Franklin et al., 2005), aramid fibers (Vallittu & Lassila, 2007; John et al., 2001), carbon/graphite fibers (Ozen et al., 2006), ultra high molecular weight polyethylene (UHMWP) fibers (Xu et al., 2003), carbon nanotubes (Singh et al., 2008) and nylon fibers (John et al., 2001) have been introduced for denture base materials to enhance the strength of denture base resins. Besides, various types of inorganic materials such as micro-fine particles serve as reinforcing components. These fillers make up the bulk of the composites and they vary in size and composition among different composites. The incorporation of silica (SiO_2), barium (Ba) and strontium (Sr) glasses in acrylic resin base materials facilitate the X-ray opacity in monitoring radiological of the composite *in vivo* (Zhou et al., 2005).

The reinforcement of acrylic resins to enhance their physical and mechanical properties is significant. The incorporation of carbon fibers improves the fatigue and tensile strengths, transverse deflection, and modulus of elasticity of PMMA resins. However, it may cause an esthetic problem because of its black color of the fibers. Metal fillers improve the thermal conductivity of PMMA and enhance its strength. Aramid fibers have significantly increased the impact strength of PMMA resin and enhance the fracture resistance of acrylic resin denture base material (Marei, 2005).

1.3 PMMA/HA composite

PMMA is one of the acrylic groups of polymers were first reported to be used as early as 1873. Self curing PMMA was developed for use as a dental material because of excellent handling characteristics and curing ability without the external heat application. PMMA is an amorphous polymer, hard and brittle at room temperature with a glass transition temperature at 105-120°C (Rehman et al., 1996). PMMA was prone to leakage and breakage because of its weak compression strength. In addition, PMMA tends to shrink after processing and it also prone to water absorption. There are some approaches used to solve this problem of PMMA.

One of the approaches to enhance the mechanical properties of PMMA is by adding filler and additives. There are a few types of filler used to reinforce PMMA, e.g., glass fiber, carbon fiber, barium particles, zirconium particles and ceramic particles. Among others, hydroxyapatite (HA) can be used to improve the mechanical, thermal, and rheological properties of PMMA. HA is a naturally occurring form of calcium apatite with the formula of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. HA is the preferred reinforcement because of its stiffness, density, and bioactivity (Cheang & Khor, 2003). HA is considered to be a biocompatible and osteoconductive material, which

exhibits an extracellular response to bone growth as the bone-filler mineral (Chouzouri & Xanthos, 2005). It has been successfully used as bone fillers, aesthetic restorative, coating of orthopedic implants filler or inorganic/polymer composites, cell-culture carries and so on (Pramanik et al., 2009).

Shinzato et al. (2000) reported that the mechanical properties of PMMA can be enhanced by the addition of HA filler. However, the amount of HA was limited to 2-20 wt%. According to Vallo et al. (2000), incorporating HA fillers into PMMA bone cement had shown increment in flexural modulus and fracture toughness. However, a high proportion of filler in PMMA matrix lead to increase of void contents, and thus reduce the strength of the PMMA/HA cement. In addition, poor adhesion and void formation between the HA and PMMA components can lead to a reduction in yield stress (Serbetci et al., 2000).

1.4 Problem statement

PMMA has been widely used as a main component of denture base polymer for many years; this material is sometimes fractured or cracked in clinical use. One of the factors that cause fracture is considered to be low resistance to impact, flexural or fatigue. PMMA is brittle, shrinkage, present of voids that further reduce its mechanical properties in clinical application such as in joint replacement and dental implants application. PMMA also undergoes an exothermic polymerization reaction which bring damage or allergic to bone tissue. HA is a well-documented ceramic has been successful used in implant applications (Moursi et al., 2002). However, the flexural strength of PMMA was decreased by the addition of HA. This is due to the agglomeration of the HA filler particles and the incompatibility HA with PMMA matrix (Chow et al., 2008). The agglomeration and incompatibility of HA will cause

existing gap between HA and PMMA and thus, lead to reduction of mechanical interlocking followed by poor mechanical properties for PMMA/HA system.

According to a survey 68% of dentures had broken within three years of the low fracture resistance of PMMA provision. It is also reported that 33% of the repairs carried out by three laboratories were due to debond or detach teeth, 29% were because of midline fractures which were more commonly seen in the upper dentures and the rest (38%) were other types of fracture. Most of the fractures had occurred in the mouth whilst chewing and majority of dentures were made of acrylic resin while some had form of strengtheners. Despite considerable efforts to improve the fracture resistance of PMMA by incorporating different chemical modifiers, fibers, metals and particles, few have obtained promising results and improve the mechanical properties of PMMA by filler particles incorporation (Nejatian et al., 2006).

For filled and unfilled polymeric materials, the water absorption is an important indicator in dental applications. Water absorption may decrease the life of resin composites by silane hydrolysis and crack formation. Excessive water uptake can promote breakdown causing a filler-matrix debonding (Santos et al, 2002). The PMMA/HA composite are easy undergoing water absorption due to the free and reactive hydroxyl groups of the HA filler which exhibit good affinity with water molecule and also present of micro-voids due to different chemical structure of PMMA and HA. The micro-voids are essential for the transportation of water molecules when soaking in an aqueous environment (e.g. water and simulated body fluid (SBF)). The water sorption of the denture base material should be as low as possible in fact to affect the dimensional behaviour and denture stability.

1.5 Hypothesis

In the preliminary work, by using planetary ball milling technique to prepare PMMA composites, the particles size of PMMA/HA powder could be reduced. The mechanical properties of PMMA composites will be expected to improve due to the increase of the volume of fine particles in the composites specimens resulting in a more homogeneous distribution of HA in PMMA system and thus a reduction of void contents in PMMA composites. Mechanical activation, as a simple and low-cost method for modifying physio-chemical properties of disperse systems, is often used in technologies for obtaining powders (Sreckovic et al., 2008). The high speed of rotation of the planetary ball milling makes the balls move strongly, leading to fine grinding of powder owing to the generation of large ball impact energy. The main purpose of this work is to prepare fine and homogeneous PMMA/HA powder using planetary ball milling technique.

Besides, there were been many studies on the mechanical problem in dental application and they are summarized in the following two approaches. The first approach is to increase the strength of denture base polymer by adding a cross-linking agent of poly-functional monomer such as poly (ethylene glycol dimethacrylate). The second approach is to devise a reinforcement of denture base polymer with fibers or rods such as metal wires or metal nets (Kanie et al., 2000). As mentioned earlier, HA is preferred reinforcing filler in PMMA matrix because of its stiffness, high density and bioactivity behaviors. Hypothetically, the addition of HA filler in amorphous PMMA polymer will achieve the strength of denture base materials.

The interaction and adhesion between the ceramic filler and the respective polymeric matrix have a significant effect on the properties of particulate filled

reinforced materials. The good interaction/adhesion of two materials is being essential to transfer the load between the two phases and thus improve the mechanical performance of the composites. Therefore, it is necessary to improve the interfacial interactions between HA and a particular polymeric matrix by using silane coupling agents, zirconyl salts, organic isocyanates and polyacids (Vaz et al., 2002). The tensile strength of the composite is strongly dependent on particle integrity whereas the elastic modulus is more dependent on interfacial bonding. It is expected that by adding coupling agents such as silane, titanate and zirconate based in PMMA/HA composite will provide good interfacial bonding between HA surface and polymer matrix. The coupling agent applied in dental resin composites is 3-(trimethoxysilyl) propyl methacrylate (γ -MPS), isopropyl triisostearoyl titanate and neopentyl(diallyl)oxy trimethacryl zirconate. The selection of these coupling agents is based on the functional group, there is containing methacrylate or ester groups which are expected to have good affinity with the PMMA. Matinlinna et al. (2004) reported that the γ -MPS has a significant role as a coupling agent provided high bond strength for bonding composite resin. Tensile properties of polyethylene/hydroxyapatite composites increase by a low concentration of zirconate coupling agent (i.e. 0.3 and 0.5 wt%) (Carmen et al., 2007). The coupling agent is capable of improving chemical bonding between two materials of the composites. The modified interface surface will reduce debonding at the filler-matrix interface leading to stronger and higher modulus material. The HA surface treatment by coupling agent will promote filler-matrix interaction and hence improve mechanical properties and fracture toughness of the composite as well as its processing capability.

It is also expected that the equilibrium moisture content (i.e. water absorption and simulated body fluid (SBF) absorption) of PMMA/HA composites will be decreased after surface treatment due to the hydrophobic behaviours of coupling and compatibility of PMMA with HA. The kinetics of moisture absorption of the PMMA/HA composites may conform to Fickian law behavior, whereby the initial moisture absorptions follows a linear relationship between the percentage gain at any time t and $t^{1/2}$, followed by saturation.

1.6 Research objectives

1. To investigate the effects of HA on the mechanical, thermal, morphological and radiopacity properties of PMMA denture base materials.
2. To study the effects of three different type of coupling agents on the mechanical, thermal and morphology properties of PMMA/HA composites.
3. To determine the effects and kinetic of water absorption and simulated body fluid (SBF) on the mechanical properties of PMMA/HA composites.

1.7 Outline of thesis structure

Chapter 1 originates with some basic information on the definition of denture base materials and brief introduction on the development of denture base followed by the used of polymers in the denture base. Issues that were of concern, which generated the ideas and inputs for this research work, are also detailed upon. The objectives and general direction of the whole research programme are also carefully outlined.

Chapter 2 relates the definition of dentures and dental base materials that used in prosthetic dentistry and types of denture base materials. Explanation on the methods of acrylic resins polymerization and focus on the curing of denture base material prior to treatment of modified acrylic materials. Subsequently, a literature review about the various published work on PMMA denture base materials those that are correspondingly to this research work is presented.

Chapter 3 comprise the step-by-step experimental procedures utilized, details of laboratory equipments used as well as processing techniques employed in generating any data that were used in this research work.

Chapter 4 reports the results and discussion of this study. It studies with the description effect of planetary grinding time on PMMA/HA powder with different grinding time on the particle size distribution of the filler particles into the polymer matrix as well as from the data graphs and charts on the mechanical properties and X-ray diffraction (XRD) analysis. Micrographs from the field emission scanning electron microscopy (FESEM) about the morphology of the fracture surface would be featured here and detailed analysis would be carried out based on the data collected. The effects of the surface treatment of the HA filler utilizing silane coupling agent, titanate coupling agent and zirconate coupling agent on the properties of PMMA is reported in second part. The properties of treated HA filled PMMA matrix would be compared extensively and their mechanical properties would be commented upon. The morphology of the fracture surface is investigated by FESEM and energy dispersive X-ray analysis (EDX). Fourier transform infrared spectroscopy (FTIR) analysis was also reported here to characterize the surface of treated fillers. The thermal properties are investigated with the numerical data and graphs obtained are also presented here. In the last part of this chapter, a detailed

analysis would be carried out based on water absorption and simulated body fluid (SBF) absorption as well as their effects on mechanical properties. The effects of HA filler on the radiopacity of denture base would be determined and compared extensively with that of the aluminum sheet by using X-ray.

Chapter 5 presents some concluding remarks on the present work as well as some suggestion for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Denture base

Removable prosthodontics same like fixed prosthodontics which refers to the replacement of missing teeth and tissues with artificial structures or prostheses. The difference is the prostheses can be removed from the mouth by the patient for cleaning, examination and repair. Removable prosthodontics consist two types of prostheses which are partial dentures and complete (full) dentures (c.f. Figure 2.1) (Christensen, 2006). Partial denture is the abutment teeth where the metal framework of the partial rests must be prepared before the final impressions are taken. The complete denture is fabricated to restore function and improves esthetics for the patient when the natural teeth are lost. The denture has two basic components which are the base and the denture teeth. The denture base is made of denture acrylic and may have a metal mesh embedded in the acrylic for additional strength. The acrylic resins are pigmented to shade the base to resemble the normal gingival. The denture tooth is used in construction of the denture which is made of porcelain or acrylic resin (Thomas & Catherine, 1987).

2.2 Development of denture base

Denture base is the material in which the teeth of a denture are set and which rests on the supporting tissues/oral mucosa when the denture is placed in the mouth. Over the past century, denture base materials have been progressed through various stages of development. Vulcanized rubber (vulcanite) was introduced to the dental



Figure 2.1 Denture (a) Complete denture, (b) Partial denture

profession in 1855. Vulcanite is an unsaturated polymer of isoprene, impregnated with 32% sulphur and used to be supplied as plastic sheets. However, it presented esthetic and dimensional change issues as well as fabrication challenges. The development of polymers used in today's dentistry, commonly known as "Dental resins" which are used in all specialties of the profession, whether restorative teeth or structures, prosthodontics (including dentures) or surgical (involving stents and supports). Therefore, polymers become inevitable part of this modern decade (Bhola et al., 2010). Poly(methyl methacrylate) (PMMA) had replaced vulcanite because of its greater physical and esthetic properties. In addition, PMMA is inexpensive and easily manipulated. After then, few of addition polymers such as polystyrene, poly(vinyl acrylic), polyamides (nylons) and light-activated urethane dimethacrylate resins have been evaluated for denture base application. PMMA resins have been shown to exhibit higher levels of impact and flexural fatigue strengths than other polymers (Machado et al., 2007).

Cellulose products, phenol formaldehyde, vinyl resins and vulcanite have been used to make dentures. Nevertheless, there are several problems have been suffered. Cellulose products are warpage easily in the mouth and a taste of camphor due to its use as plasticizer. Therefore, the leached out camphor from the denture

will cause blistering, staining and loss of color within a few months. Phenol formaldehyde (Bakelite) is difficult to process and will lose its color in the mouth. Vinyl resins were found that have low fracture resistance and it possibility due to fatigue. Vulcanite was the first material used to produce denture. However, its aesthetic qualities are not very good and it has now been replaced by acrylic resins (Noort, 2002a).

According to Meng & Latta (2005), denture failures occur excessively in thin areas or weakened flanges around frenal notches. There was recommended that increase the bulk of material in regions include the palatal incisal junction, the posterior palatal midline and the mandibular incisal area adjacent to the lingual and labial frenal attachments where subject to deformation and fractures. However, a denture base becomes too thick when the increasing the bulk of material which can cause gagging or dislodgement of the denture when the patient opens wide of yawns. While minimizing the thickness of denture base can lead to better patient acceptance, it is also increase the potential for fracture making the use of a stronger acrylic resin very significantly.

2.3 Types of denture base materials

The most common denture base polymer is dental acrylic or PMMA. There are used in individual impression trays and orthodontic devices, in addition to dentures and artificial crowns. The dental acrylic has essentially the same composition as commercial Plexiglas but the pigmented and processed are differently. The development of prosthesis and implants made from polymer has been in use for the last three decades. Methylesters of methacrylic acid are the basic constituents of PMMA but several additions are made as their properties and applications to get the

desired characteristics (Bhola et al., 2010). The dental resin with same composition can be differentiated by different processing method, such as conventional curing method by application of heat, self-curing reactions, light polymerization and microwave energy application.

2.3.1 Classification of polymeric denture base materials

Polymeric denture base materials are classified into five groups or types as showed in Table 2.1 which according to ISO 1567:2000. Table 2.2 shows the requirements of denture base polymers in according to ISO 1567:2000. The ISO classifies denture base polymers and copolymer to specific their requirements and the test methods to be used in determining compliance with these requirements.

Table 2.1 Classification of denture base polymers according to ISO 1567:2000

Types	Class	Description
1		Heat-polymerizable polymers
	1	Powder and liquid
	2	Plastic cake
2		Auto-polymerizable polymers
	1	Powder and liquid
	2	Powder and liquid pour-type resins
3	-	Thermoplastic blank or powder
4	-	Light-activated materials
5	-	Microwave cure materials

Table 2.2 Requirements of denture base polymer as given in ISO 1567:2000

Parameter	Type of denture base material	
	1,3,4,5	2
Flexural strength (MPa) min.	65	60
Flexural modulus (MPa) min.	2000	1500
Residual methyl methacrylate monomer (% wt) max.	2.2	4.5
Sorption ($\mu\text{g}/\text{mm}^3$) max.	32	32
Solubility ($\mu\text{g}/\text{mm}^3$) max.	1.6	8.0

2.3.2 Composition of acrylic denture base materials for Type 1 and 2 materials

Table 2.3 shows the denture base materials are composed in powder form and liquid phases. The polymer powder comprises beads of PMMA and colouring additives are added to characterise the oral tissue which is further enhanced by addition of nylon or acrylic fibers to mimic the blood vessels and capillaries found in the oral mucosa. PMMA prepolymerized beads are mix with the monomer, during which are wetted by the monomer lead to dispersion of some polymer chains in the monomer. Accordingly, the viscosity of the mixing will be increased. Mixing are then gives a sand like consistency initially, which progresses to a stringy paste, subsequently the number of polymer molecules in solution increase. Thus, there is forming a pliable dough-like paste. The dough at this stage loses its lacking and is ready for compression molding. Besides, the cross-linking agents such as ethylene glycol dimethacrylate are added to improve hardness and wear resistance of the product (Deb, 1998).

The polymerization mechanism involves the conversion of monomers to polymers, in both the heat and auto curing reactions. Decomposition of the initiator (primarily dibenzoyl peroxide) into free radicals under heat, initiates chain

propagation for a heat activated reaction. Polymerization of chemically curing acrylics is triggered via a redox reaction occurring at the oral temperature, mainly under the influence of an accelerator (i.e. primary amine, sulfinic acid or substituted barbituric acid), comprising the amine-peroxide redox system (Bhola et al., 2010).

Table 2.3 Compositions of poly(methyl methacrylate) denture bases (Deb, 1998)

Powder	Liquid
Poly(methylmethacrylate) PMMA powder	Monomer: methyl methacrylate
Benzoyl peroxide (initiator)	Cross-linking agents, hydroquinone (inhibitors)
Pigments (organic dyes)	Tertiary amine activator

2.3.2(a) Conventional heat-cured poly (methyl methacrylate) (PMMA)

Conventional heat-cured PMMA is provided as a powder and liquid. The powder form contains a copolymer of PMMA in the form of spheres or beads which the benzoyl peroxide (BPO) initiator is added. The BPO creates the first free radicals that initiate the polymerization chain reaction by opening the double bond of the methyl methacrylate. The thermal reaction above a temperature 60°C generates free radical and the exothermal polymerization reaction has a tendency to propagate as the temperature increase (Ming et al., 1996). The PMMA is polymerized to a very high molecular weight. The liquid is methyl methacrylate (MMA) monomer with a cross-linking agent (usually 5 to 15% ethylene glycol dimethacrylate) and a small amount inhibitor such as hydroquinone to avoid premature polymerization and enhance shelf life. The cross-linking molecules are added to reduce the 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

(Ferracane, 2001). Regardless of combination of polymerization of conversion of methyl methacrylate to PMMA and the curing process used, the conversion is not complete and there is a certain amount of residual monomers, such as MMA, in the polymer. The residual MMA in a dental acrylic resin had deleterious effects on many of its properties such as water absorption, hardness, dimension stability, tensile strength, flexural strength, and biocompatibility (Bayraktar et al., 2005).

MMA is a flammable liquid of low viscosity. It is extremely volatile and boils at approximately 100°C. When it polymerizes, it shrinks approximately 20% by volume. It can be a physical irritant to the skin, producing an itching feeling know as allergen. A correctly heat-processed denture base could have as little as 0.3% to as much as 2% residual MMA monomer. The high temperature at which conventional dentures are processed ensures a thorough polymerization although there are not complete. Besides, the high processing temperature will also lead to a greater dimensional change, resulting in shrinkage of approximately 0.4% across the molar region (Ferracane, 2001).

In the conventional heat-cured method, the monomer molecules are moved by thermal shocks that receive from other molecules. Thus, they are passively moved and their movements are consequence of the outside heat (Nilufer et al., 2008).

2.3.2(b) Cold-cured poly (methyl methacrylate)

Cold-cured is known as self-curing or so called autopolymerization which is often referred as “pour resin” because it is poured into a processing mold made of agar hydrocolloid to form a denture base. Autopolymerized acrylic resin is either bench-cured at room temperature (~20°C) or, more frequently, hydroflask-cured in warm water. It is well known that residual monomer content in autopolymerized

resin specimens is higher than in their heat-polymerized counterparts (Bayraktar et al., 2005). The composition of this material is the same as the heat-cured version with two differences:

- (1) The powder contains beads of polymer that have a lower molecular weight than those of the heat-cured material
- (2) The liquid contains a chemical activator (an amine molecule) such as dimethyl-p-toluidine) 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 a lower dimensional change (0.2%) than dentures produced by heat processing (Ferracane, 2001).

The resistance to plastic deformation of a denture base can be significantly decreased after relining because of autopolymerizing resins present lower mechanical strength when compared with heat-polymerized denture base resins. The higher residual monomer content in the autopolymerizing acrylic resins is the low degree of conversion achieved by the use of chemical activation, as opposed to that generated by heat activation (Vergani et al., 2005).

2.3.2(c) High impact resistant acrylic

This denture base resin is similar to the heat-cured material and is processed the same way but it has much higher impact strength. Therefore, it is less likely to be accidentally broken if dropped by the patient compare to conventional material. These resins are produced by substituting the PMMA in the powder with a copolymer. The copolymer is form with rubbery monomer that provides the material to behave as internal shock absorber. The materials have high impact resistance, low crazing and fit in a way comparable with that of the conventional materials

(Ferracane, 2001). Resilient denture lining materials have been used in dentistry for many years. Silicone-based materials were introduced in 1958. Polydimethyl siloxane is a viscous liquid that can be cross-linked to form an elastic rubber and no plasticizer is necessary. This material is used for patients unable to tolerate the hardness of a heat-polymerized acrylic denture base (Mese & Guzel, 2008). Dispersion of rubber-based composite particles in PMMA matrix allows that tension generated by impact propagate through the material, losing acceleration and improving in the rubber/PMMA interface. The incorporation of rubber can absorb more energy generated by impacts, avoiding fractures and allowing that the prosthetic device function for longer periods. The fracture resistance of high-impact PMMA was twice than those of the conventional resins (Pires-de-Souza et al., 2009).

2.3.2(d) Injection-molded polymers

Acrylic resins have been modified to improve to their physical and chemical properties and also their working properties to aid the laboratory in the processing of complete dentures. According to Nilufer et al. (2008), the injection molding method allows directional control of the polymerization process through the flask design. A constant flow of new material from the sprue compensates for the polymerization shrinkage and produces a more accurate denture compared to that produced by the compression molding method. Karacaer et al. (2003) reported that the injection molded specimens with the 5% loading of fiber, the transverse strength increased about 35% and the elastic modulus increased approximately 48% compare to that of compression-molded specimens.

Injection-molded polymers are usually made of nylon and polycarbonate. The material is in the form of gel and must be heated and injected into a mold. The

equipment for processing these polymers is more expensive than that for processing conventional denture resins. The craze resistance of these materials is not equivalent to that of the conventional acrylic. These polymers exhibit high impact resistance and do not contain MMA monomer and suitable used for patient who are allergic to MMA (Ferracane, 2001). However, nylon had limitation advantages, such as warpage, water absorption, discoloration, surface roughness, bacterial contamination, and difficulty in polishing (Parvizi et al., 2004).

2.3.2(e) Rapid heat-polymerized polymers

The denture base resins used with rapid heat-polymerized polymers are the same as the conventional materials, but they contain a chemical activator in the monomer formulation. The activators react with the initiator in the powder, the activators was consumed and reducing its availability. Therefore, polymerization of the monomer is less efficient and residual monomer is left in the resin (Sato et al., 2005). The initiator allows them to be processed in boiling water for 20 minutes which is faster processing compare to conventional heat-curing method. The rapid heat polymerization process is processed on the automatic control pressure equipment (less than 6 kgf/cm² pressure with the water at 120°C for 10 minutes) was completely polymerized. The lower porosity could be attributed to the role of pressure accelerating the polymerization. The higher pressure is instantly transmitted to the resin dough and prevents the monomer from boiling (Ming et al., 1996).

A problem has occurred with these dentures is that areas of the base thicker than approximately 6 mm have a high level of porosity. A correctly processed conventional acrylic should have little porosity up to a thickness of almost 20 mm. The short duration of the heating also leaves a higher level of residual monomer,

three to seven times greater than that of conventionally heat-cured denture base (Ferracane, 2001). Mechanical properties might be adversely affected by high levels of residual monomer because of a plasticizing effect of the monomer resulting in reduces interchain forces and yields easier deformation under load (Sato et al., 2005).

2.3.2(f) Microwave-polymerized polymers

The resins used with microwave-polymerized polymers have the same composition which used in conventional material. Properties of microwave-polymerized polymer are optimal when a special liquid is substituted for the normal monomer liquid. The denture base cures well in the special polycarbonate flask with normal monomer liquid but it shows a higher level of porosity than dentures processed with the special liquid. The properties and the accuracy of these resins have been show to be better than those of the conventional heat-cured resins and the processing time are much shorter (4 to 5 minutes) (Ferracane, 2001). The microwave irradiation may increase the degree of conversion of authopolymerized resins thus enhancing their mechanical properties (Blagojevic & Murphy, 1999).

The greater advantage of microwave heating over conventional heat is that temperature rises fast. The microwaves can be easily surpassed to heat the monomer over than temperature 100.8°C. Thus, the temperature must be monitored and controlled accurately. The external porosity can be observed when the acrylic resin specimens have absorbed too much energy at the beginning of the polymerization. The internal porosity occurred when too much energy was applied at the end of polymerization using microwave energy. Therefore, the porosity in microwave-polymerized specimens can be reduced by a longer polymerization time at lower wattage (Barbosa et al., 2007).

According to Nilufer et al., (2008), the use of microwave energy to polymerize PMMA was become popular as an alternative to conventional water-bath processing. This method has been shown to be an efficient source of electromagnetic energy to polymerize acrylic resin dentures. A high-frequency electromagnetic field will expose the vibration of monomer molecules and their movements are the cause of the internal heat. The collisions of intermolecular will generate the heat for the activation process. Therefore, it is possible to process acrylic dentures in a very short time as the surface and the deeper parts of the resin are uniformly and rapidly heated with less equipment required. Microwave energy used for polymerization, having the advantage of reduced time for curing, a smaller time for obtaining of the plastic phase, a bigger homogeneity of the mixture and the achievement of a prosthetic material with excellent mechanical strength (Patil et al, 2009). Besides that, the temperature increase, the movements of molecules become faster and the more complete the polymerization reaction and therefore less residual monomer release.

2.3.2(g) Light-activated polymer

Light-activated polymer is a composite, consisting of a paste of urethane dimethacrylate monomer with fillers. It is used as a denture base resin, as a repair material for prosthodontics and as a custom tray material. Some studies have shown the properties of light-activated polymer is slightly lower than those of the conventional PMMA materials and produce slightly rougher surfaces that seem to stain more steadily. However, one study showed their fit to better than that of conventional heat-cured resins, although not quite equivalent to cold-cured or microwave-processed dentures (Ferracane, 2001). The photoactivated resin ETHM consists of urethane dimethacrylate, triethylene glycol dimethacrylate (TEGDMA)

and 2-hydroxy ethyl methacrylate (HEMA) with photoinitiator system is photopolymerized by irradiating sequentially each face the mold with visible light (O'Donnell et al., 2008). When these materials used as a repair material, its transverse strength was found to be inferior compare to that of traditional autopolymerized resins. It demonstrates poor cohesion or adhesion to PMMA resins (Gorman & O'Sullivan, 2006).

The visible light-polymerization denture base material has less change in vertical dimension shrinkage in comparison to dentures process in compression molding, heat-polymerized, acrylic resin denture base. However, the failure of the bond between acrylic resin teeth and visible light-cured denture base materials remains a considerable problem. This visible light-cured resin is made of light-polymerizing urethane dimethacrylate which do not contain methyl, ethyl, propyl or butyl methacrylate monomers. Thus, no residual monomer is contained in the definitive prosthesis (Grossmann & Savion, 2005).

2.3.3 Requirements for a denture base

The requirements for a denture polymer can be categorized into physical, aesthetic, chemical, rheometric, thermal, and biocompatibility properties (Bhola et al., 2010).

i) Physical properties

A denture polymer should possess adequate resilience resistant and strength to biting, chewing, impact forces and excessive wear under mastication. It should be stable under all conditions of service, including thermal and loading shocks.

ii) Aesthetic properties

From the aesthetic, the resin should exhibit sufficient translucency and transparency (hue and chroma) to match the adjacent structures and tissues. Once fabricated, the denture polymer should maintain the appearance and color and not change subsequently.

iii) Chemical properties

Besides, the denture polymer should be chemically stable and preferably polymerize to completion, without leaching any residual monomers or chemically inert. It should be naturally insoluble in oral fluids, acid or alcohol substrates.

iv) Thermal properties

The glass transition temperature (T_g) of a plastic is one of the very significant points in determining the critical temperature in clinical properties. Polymers normally show a large variation in their properties with temperature. At sufficiently low temperatures, amorphous polymers are hard and glass-like, compared to softer and more flexible, when a critical temperature is reached usually at the glass transition temperature (T_g). Therefore, the denture polymer should be able to withstand higher temperature when the denture polymer surface contacts with hot water.

v) Biocompatibility

Biocompatibility is the ability of a polymer material or a device to remain biologically inert during functional period. Toxicity is usually manifested by the release of several chemical constituents from the material, such as residual monomer and initiator radical which may cause an allergic response in terms of localized stomatitis/dermatitis, severe toxicological reactions in patients' oral cavity. The dental resins should be non-toxic, non-irritating and otherwise non-detrimental to oral tissues. To fulfill these requirements, they should be preferably insoluble in