SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

PROPERTIES OF DIFFERENT FILLERS IN ACRYLIC RESIN FOR DENTURE APPLICATION

By

TAN JIA SHENG

Supervisor: Profesor Dr. Ir. Mariatti Bt. Jaafar @ Mustapha

Dissertation submitted in partial fulfilment
of the requirement for the degree of Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

JUNE 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Properties of different fillers in acrylic resin for denture application**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

Name of Student	: Tan Jia Sheng	Signature:
Date	: 22 June 2017	

Witnessed by

Supervisor	: Profesor Dr. Mariatti Bt. Jaafar	Signature:
Date	: 22 June 2017	

ACKNOWLEDGEMENTS

First and foremost, I would like to take this golden opportunity to thank School of Material and Mineral Resources Engineering of Universiti Sains Malaysia, which provide the sufficient resources, instrument and facilities for my project. Moreover, I would like to thanks the Dean of School Prof. Dr. Zuhailawati bt Hussain who allow me to use those resources, interment and facilities in School of Material and Mineral Resources Engineering.

In addition, I would like to express my utmost gratitude and appreciation to my final year project supervisor, Profesor Dr. Ir. Mariatti Bt. Jaafar @ Mustapha for the constant guidance, gracious support and encouragement. Besides, I am appreciated with the valuable time and effort from Professor in sharing her knowledge and experience.

Furthermore, I am really cherished the help form technician from School of Material and Mineral Resources Engineering, Universitis Malaysia, especially Encik Mokhtar, Encik Rashid, Encik Farid, Encik Sofi, Encik Norshahrizol, and Encik Helmi. I would like to thank for their guided in handling the experiment equipment throughout the project. Besides with their assistance and cooperation provided, I able to complete my final project successfully.

On the other hand, I am grateful to have help, guidance and support from post graduate student from Profesor Dr. Ir. Mariatti Bt. Jaafar @ Mustapha especially for Kak Ervana, Kak Mahira, Kak Fadilah and Lim Kai Sheng. With the guidelines from them I able to run my final project effectively.

Lastly, I would like to take this opportunity to thank my friend and family who provide endless physical and mental support throughout my final year project. Thank for their indirect support and idea, so that I able to success my project smoothly.

TABLE OF CONTENTS

Contents **Page**

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

PMMA	Poly(methyl methacrylate)
MMA	Methyl methacrylate
HA	Hydroxyapatite
β-TCP	Beta Tri-calcium Phosphate
NBR	Nitrile Butadiene Rubber
Al_2O_3	Aluminium Oxide
PLA	Polylactic Acid
BPO	Benzoyl Peroxide
EGDMA	Ethylene Glycol Dimethacryate
PS	Polystyrene
PE	Polyethylene
ZrO_2	Zirconia Dioxide
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscope
ASTM	American Society for Testing Materials
FS	Flexural strength
FM	Flexural modulus
FT	Fracture toughness
IS	Impact strength
YSZ	Yttria Stabilized Zirconia

LIST OF SYMBOLS

wt%   Weight Percentage

D_{50} Mass median diameter

SIFAT-SIFAT PENGISI YANG BERBEZA DALAM RESIN AKRILIK BAGI APIKASI GIGI PALSU

ABSTRAK

Asas gigi yang dihasilkan oleh resin akrilik biasa digunakan kerana sifat fizikal dan estetikanya yang baik. Projek ini bertujuan untuk mencari pengisi dan pembebanan pengisi yangpaling sesuai untuk meningkatkan kualiti resin akrilik. Sifat-sifat mekanik komposit PMMA telah diukur berdasar sifat lenturan, keliatan patah, kekerasan dan kekuatan hentaman. Saiz dan bentuk zarah bagi pengisi telah dianalisa. Komposit PMMA dicampur dengan menggunakan mangkuk Stryker Mixevac III di bawah keadaan vakum. Pada peringkat pertama, ujian mekanikal telah dijalankan untuk menentukan pengisi dan peratusan berat yang paling sesuai antara pengisi HA dan pengisi β-TCP. PMMA/2% HA komposit menunjukkan sifat-sifat yang paling baik. Oleh itu, dalam peringkat kedua, PMMA/2% HA komposit telah diubahsuai dengan NBR dengan peratusan berat yang berbeza. Sifat-sifat mekanikal, kestabilan haba dan penyerapan air telah diukur dalam bahagian ini. PMMA/2% HA/NBR tidak menunjukkan peningkatan yang ketara dalam sifat-sifat mekanikal. Walau bagaimanapun PMMA/2% HA/NBR dapat meningkatkan kestabilan haba dan mengurangkan penyerapan air. Pada peringkat ketiga, PMMA/2% HA ditambah dengan pengisi hibrid iaitu 2% PLA microsphere, 2% Al_2O_3 yang tidak dirawat dan 2% Al_2O_3 yang telah dirawat. Sifat-sifat mekanikal telah diukur. PMMA/2% HA/2% PLA microsphere menunjukkan peningkatan kecil dalam kesan kekuatan dan keliatan patah manakala PMMA/2% HA/2% Al_2O_3 yang telah dirawat menunjukkan peningkatan kecil dalam kekuatan lenturan. Kesimpulannya, 2% HA pengisi dapat meningkatkan sifat-sifat mekanikal komposit PMMA dengan ketara dan sifat komposit boleh ditingkatkan lagi dengan pengisi hibrid.

PROPERTIES OF DIFFERENT FILLERS IN ACRYLIC RESIN FOR DENTURE APPLICATION

ABSTRACT

Dental base which fabricated by Polymethyl methacrylate (PMMA) resin are commonly used due to its good physical and aesthetic properties. In this project, the aim is to identify the most suitable filler and optimum filler loading to improve PMMA resin properties. The mechanical properties of PMMA composites were determined based on flexural properties, fracture toughness, hardness and impact strength. PMMA composites were mixed by using Stryker Mixevac III bowl under vacuum condition. In the first stage, mechanical testing was carried out to determine the most suitable weight loading percentage between HA and β-TCP fillers. PMMA/2% HA composite showed better improvement than other filler loadings. Hence in the second stage, PMMA/2% HA composite was modified by various weight loading percentage of NBR and the mechanical properties, thermal stability and water absorption were measured. It is observed that no significant improvement in mechanical properties was obtained by adding NBR in PMMA/2% HA. However addition of NBR is able to increase the thermal stability and reduce water absorption. In third stages, PMMA/2% HA was added with hybrid fillers where 2% HA was hybridized with 2% PLA microsphere, untreated Al_2O_3 or treated Al_2O_3. PMMA/2% HA/2% PLA microsphere showed small improvement toward impact strength and fracture toughness while PMMA/2% HA/2% treated Al_2O_3 showed improvement in flexural strength. In conclusion, 2% HA filler able to increase the mechanical properties of PMMA resin significantly and the properties can be further improved by hybrid fillers

CHAPTER 1

INTRODUCTION

1.1 Research Background

Denture base is defined as the part of denture that rests on the foundation tissue and which teeth are attached. While denture base material is any substance of which a denture base maybe made. According to Vishal (2014), denture base resins are classified into 3 categories. First, they can be classified into non-metallic (acrylic resin and vinyl resin) and metallic (cobalt chromium, gold alloys and stainless steel). Second, they can be classified into temporary form (self-cure, shellac base plate, base plate wax and injection molded resins) and permanent form (heat cure denture resins, light cured resins and pour type resins). Third, they are based on ANSI/ADA classification (Sp.No 12/ ISO 1567) which are heat polymerizable polymers, auto-polymerizable polymers, thermoplastic blank or powder, light activated materials and microwave-cured materials (Vishal et al., 2014).

There are some requirement for idea denture base resin. Firstly, it must be physiologic compatibility which mean nontoxic, noncarcinogenic and nonallergenic. Secondly it must achieve acceptability to patients' senses, for example color stable, odorless, tasteless and light in weight. Third, the denture base resin must be cost effective, which include raw material, equipment for processing, cost of fabrication and good shelf life. Fourth, it must achieve certain properties such as adequate mechanical properties and satisfactory thermal properties. So that, it would not influence oral function or mechanical destruction. Fifth, hygienic factor also one of the main requirement which consist of sterilizable, nonporous to microorganisms, low fluid absorption and easy be cleaned.

Finally, the durability of denture base resin need to be high enough in oral environment. These include dimensionally stable, good bonding between base and teeth, resistant to weak acids and alkaline and resistant to abrasion and wear (McCabe & Angus, 2008).

Since first polymerized by Walter Bauer in 1936, acrylic resin denture base gradually took the place of traditional metal base and became the most commonly used denture base material in clinical fabrication (Rajul & Romesh, 2015). However, Poly-methyl methacrylate (PMMA) is still the most predominantly used denture base material in present because of low cost, light weight, insoluble in mouth fluid, excellent aesthetic properties and ability to be repaired easily (Rama et al., 2013).

Nonetheless, PMMA resin has some negative problems such as polymerization shrinkage, weak flexural, lower impact strength, and low fatigue resistance (Mahroo & Rashin, 2015). Hence there are few methods proposed by Mallikarjuna et al. (2015) to improve the properties of PMMA resin such as:

- Using polycarbonates and polyamides as substitutes for PMMA.
- Chemical modification of PMMA by the addition of copolymers, cross-linking agents and rubber substances in the form of butadiene styrene
- The incorporation of fibres, metal or ceramic inserts into the denture bases act as filler.

According to Rajul & Romesh (2015), adding filler to reinforce PMMA properties is considered the most cost effective and reasonable method. Those fillers are included in resin, metal and ceramic form to increase the mechanical, thermal and chemical properties of PMMA. However, improvement of polymer composite property depends on the filler concentration, filler morphology, degree of dispersion, orientation and degree of adhesion with the polymer matrix. Some of the materials from these developments have an excellent balance of impact resistance and flexural properties. However, most are not acceptable to the dental technician because of their processing characteristics. The most popular material at present for the fabrication of dentures, which has a high impact strength, is a rubber modified acrylic polymer whose handling characteristics are more or less identical to conventional poly (methyl methacrylate) (Rajul & Romesh, 2015).

1.2 Problem Statement

Various researchers have considered ceramic, polymer and metallic base fillers to reinforce PMMA resin for denture base material. Selection of filler is very important since some filler are not suitable to be used due to certain problem such as poor biocompatibility and biosafety, poor adhesion, lack of interaction between filler and resin, poor aesthetic properties and low mechanical and thermal properties.

PMMA is a polymer which consist of inferior mechanical strength, brittleness and low thermal conductivity. Hence low impact strength and fracture toughness are the main problem faced by PMMA as denture based materials. Besides, high water sorption of PMMA is also a problem which will cause polymerisation shrinkage and affect the dimension of denture base material. In order to solve these problem, various type of fillers such as hydroxyapatite, beta tri-calcium phosphate, nitrile butadiene rubber, polylactic acid microsphere, untreated alumina and treated alumina are added to solve the problem faced by dental base material.

1.3 Objective

- To investigate the effect of different type of fillers hydroxyapatite (HA) and beta tri-calcium phosphate (β-TCP)) and it's loading on the properties of PMMA denture base composites.

- To study the effect of Nitrile-Butadiene Rubber (NBR) addition on the properties of PMMA denture base composites
- To study the effect of PMMA reinforced by hybrid fillers (HA with addition of polylactic acid (PLA) microsphere, treated Al_2O_3 or untreated Al_2O_3) on the properties of PMMA denture base composites.

1.4 Thesis Outline

Chapter 1:	Discussed on the introduction of dissertation including background of denture base materials, problem statement, objectives of this work and the scope or this project.
Chapter 2:	Discussed on the overview survey of literature on the denture base materials, filler used and their role and properties in reference to widely relevant to the previous works or research that are closely related to this study
Chapter 3:	Discussed about the raw materials being used in this project and the methodology of this project. The characterization methods used in this project also stated in this chapter.
Chapter 4:	Discussed the results and findings of the experimental works done and synthesizing the information on the usefulness of reinforcing method in this study.
Chapter 5:	Discussed on the conclusion and the recommendation for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Since ancient origin 5000BC, people need prosthesis contemporary materials for dental application. This is because, the loss of teeth may due to dental disease, pathology, trauma or accident has plagued mankind throughout the ages. Hence to restore the exterior need and interior function, it is required other materials to replace its application.

In dentist field, civilization has progressed in order to improve the quantity and quality of dental base. Hence, up to now there are several available materials are still under research to achieve its ideal properties. The civilization in prosthesis dental base include the development of biological, chemical and physical sciences. The denture base materials should be biological compatible, light weight, readily available, cost effective, simple fabrication process in order to develop a prosthesis that is functionally effective, nice appearance and non-toxic.

2.2 Materials and development for denture application

Before 18th century, Japanese were masters the art of wood carving in making wooden denture, while George Washington also had a set of dentures which made from wood (William, 2017). Wood had been used on that period because it was readily available, inexpensive and could be carved. However due to some drawbacks, wood was considered not the good to be used as denture base material. For examples, it was cracked easily in moisture, not aesthetic, unhygienic and degraded in mouth. The further development of denture base was slow until 17th century, Pierre Fauchard discovered teeth made from hippopotamus, bone and elephant ivory (Monsieur, 2017). Bone displayed better dimensional stability compared to wood although the aesthetic and hygienic concerns were remained. Ivory shows more stable in the oral environment and offer significant aesthetics. However, it was not readily available and not cost effective.

During 18th century, the development of denture base materials started by using gold and porcelain. In year 1775, French dentist Etienne Bourdet made the first reference to the use of a gold base punctuated with small holes much like the sockets of teeth (Lang, 1974). Gold base material show more resistant to deformation and less porosity high strength and accuracy of fit complement the reduction in base deformation. This prevented excessive loss and the supporting structure (Brien et al., 1974). In year 1788, Alexis Duchateau and his team Parisian dentist Nicholas Dubois De Chemant successfully made a baked porcelain complete denture in a single block. At that period, ivory, bone and animal substances were replaced by porcelain. This is because, porcelain able be shaped easily, extremely stable, low water absorption, low porosity, low solubility and ensured intimate contact with the underlying tissues. Besides the colour of porcelain was quite like the colour of teeth and oral soft tissue. However, porcelain was faced difficulty in dimensional stability due to resist distortion during firing, brittleness and difficulty in grinding and polishing (Samuel, 1995).

During the latter part of the 19th century, polymers were entered denture base material field. In year 1839, Charles Goodyear was developed the art of rubber and his brother Nelson Goodyear invented vulcanite which consist as hard rubber. The introduction of vulcanite into dentistry brought the development of denture base step into higher level. The appearance vulcanite dentures were fitted the ridges of patient. Besides, it was more economy, higher durability, light weight and easier to fabricate. In 19th century, others than vulcanite rubber, there were other materials under investigation. For example, CF Harrington introduce tortoise shell base in year 1850, Edwin Truman introduce Gutta percha in year 1852, Alfred used low fusing alloy such as silver, bismuth and antimony in year 1856, Dr Bean discovery Aluminium base in year 1867, John Wesley Hyatt used cellulose nitrate in his first organic plastic molding compound in years 1868 and used it as denture base material in years 1870 (Khindria et al., 2017).

After discovered acrylic resin as denture base material by Walter Bauer in 1936, it was represented such significant improvement in dental. In 20th century, there were estimated 95% of all dentures were fabricated by using methylmethacrylate polymer. However, there were still other denture base materials were discovered on that period. For example, Dr. Leo Bakeland used bakelite in 1909 as denture base material. Although it was high availability, but it was lack of uniformity, poor colour quality and difficult to repair. During year 1930, mixtures of polymerized vinyl chloride and vinyl acetate were available, with pleasing colour but the processing methods were difficult. In year 1948, Charles Dimmer introduced vinyl acrylic copolymer polystyrene as denture base materials. Both of the materials were great in transverse and high residual stresses. Others than these, there were still others denture base materials were discovered such as stainless steel, cobalt chromium, epoxy resin, polystyrene, nylon polycarbonates and polysulphone (Khindria et al., 2017).

Until today, there are some scientist still finding the most suitable denture base materials. However, the improvement of acrylic resin in denture field also played an important role. Researcher and scientist were searching the best way to modify or reinforce acrylic resin to achieve denture base ideal properties.

2.3 Denture base material

Since early centuries different base materials had been used to make denture base, which include polymer, metal and ceramic. However, every material had its own advantage and weaknesses. In current stage, although acrylic resin is the most suitable material used for dental base, but it also not considers as an idea material. It still had weakness. Hence there were several ways able to restore the defect and improve the properties.

2.3.1 Polymer

Polymer is a large molecule or macromolecule composed with repeated unit. They may be formed by condensation polymerization or addition polymerization. Acrylic resins are polymer esters of methacrylic acids. Among these, PMMA is one of the common polymer used as denture base material. It is a thermoplastic which can be heated and manipulated repeatedly. PMMA is the combination of methyl methacrylate with chemical formula $(C_5H_8O_2)_n$. Figure 2.1 show the structure of PMMA before polymerization and after polymerization.

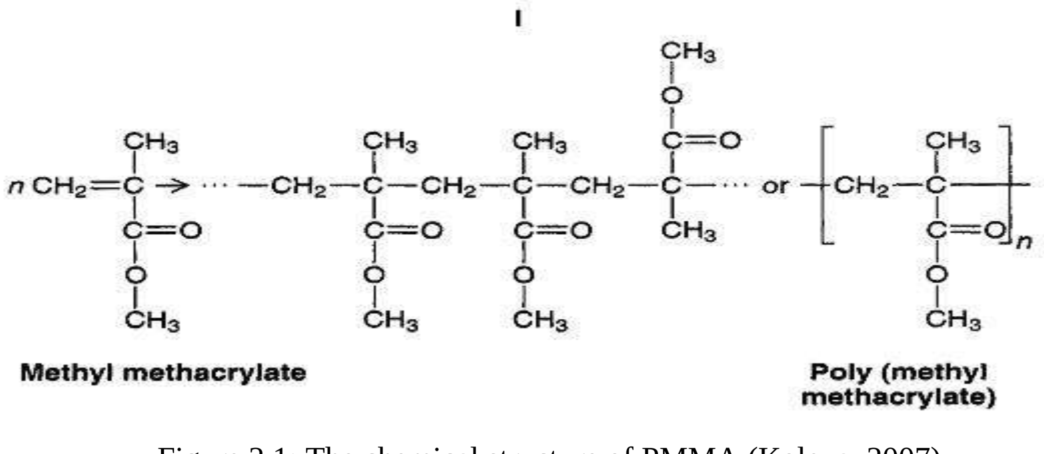

Figure 2.1: The chemical structure of PMMA (Koleva, 2007)

PMMA is linear thermoplastic polymer which lack of methyl group on its backbone carbon chain. Due to its long polymer chains are thinner and smoother which may side pass to each other, hence the original PMMA are softer. For dental material used, the composition is mixed from acrylic polymer powder, methyl methacrylate monomer which is a thin liquid, and usually an organic peroxide hardener of some sort (Andrew, 2017). PMMA has several advantages such as excellent aesthetic characteristic, adequate strength, easy repair, low water absorption and solubility and simple fabrication process. However, PMMA also faced some drawback such as polymerization shrinkage, low impact strength, low fatigue resistance and weak flexural (Athar et al., 2009).

Polyamide resin was proposed as a denture base material in year 1950 (Watt, 1955). Polyamide is a thermoplastic polymer which under part of nylon. The formation of polyamide is based of condensation reactions between diamine $N_2H_4(CH_2)_6$ and dibasic acid $C_2O_4H_2(CH_2)_4$. Polyamide is a crystalline polymer which the crystalline effect accounts for the lack of solubility in solvent. Besides it has high heat resistance, high strength couple with ductility, high elasticity than common polymerizing resin and non-toxic. The polymerization shrinkage of polyamide can also be control by using heat-molding method (Mahroo & Rashin, 2015). However, it has some drawback such as water absorption, surface roughness, warpage colour deterioration, bacterial contamination and difficult in polishing (Yunus et al., 2005).

Acetal was first proposed as an unbreakable thermoplastic resin removable partial denture material in year 1971. Thermoplastic acetal as a homo-polymer, it has good short term mechanical properties, however as a copolymer, acetal has better long term stability (Shivani & Shekhar, 2013). The homo-polymer of acetal is poly(oxymethylene) which is a chain of alternating methyl group linked together by an oxygen molecule, while for co-polymer for acetal which have been developed with are polycarbonate and polyurethane.

Acetal resins are formed by the polymerisation of formaldehyde. These resins are hard, rigid tough, low coefficient of friction, high fatigue resistance and good biocompatibility materials. However, under fluid environment, it may deleteriously affect the stress resistance and implication for the use of these resins (Fitton et al., 1995).

Polystyrene (PS) is one of the polymer which can be used for denture base application (Camilo et al., 2007). In year 1948, polystyrene was developed by Charles Dimmer, and were introduced as denture base material. Polystyrene had great transverse and high residual stress. However, it had not been uniformly used as denture base material due to lack of flexibility and strength. Although those properties can be obtained by injection molding method, but this method required very high pressures which unable to withstand by denture molding (Dresch, 1944). Polystyrene is also a versatile plastic used to make a wide variety of consumer products. In addition, it also made into foam material, which called expanded polystyrene (EPS) or extruded polystyrene (XPS), which is valued for its insulating and cushioning properties (Khindria et al., 2017).

2.3.2 Polymer composite

Polymer composite is a combination of two or more chemically different materials with a distinct interface between them. Although the constituent materials maintain their separation identities in the polymer composite, however the combination show the properties and characteristics that are different from those of the constituents. For polymer composite the continuous phase is polymer bases matrix, while the discontinuous phase which is the reinforcement part can be either in polymer, metal or ceramic bases. The reason of polymer composite exists due to pure polymer show some disadvantage in term of service life, mechanical properties and thermal properties. In order to improve the shortage of pure polymer, different bases of fillers are added to the polymer to improve the specific properties and reduce the costs needed for a product. In addition, to enhance the properties of composites, reinforcement surface may be treated chemically or coated with a very thin layer of chemicals. These methods are to improve the wetting and interfacial bonding between matrixes and reinforcements. Other than that, the surface treatment also may serve to protect the reinforcement surface from degradation by environmental attack (Mallick, 1997).

2.3.2 (a) Types of matrix

In this study, polymer base material had been chosen to be the matrix part of denture base. Started from 19th century, there are several polymers had been used as denture base material. Among those polymers, PMMA were the most commonly used denture base material since its being introduced by Walter Bauer in year 1936 (Catherine, 2010). After year 1940, PMMA is the commonly used material to fabricate denture base by heat-curing technique. PMMA has the advantage of cost effective, simple fabrication process, lightweight, satisfactory aesthetics, and easy to do finishing and polishing, although it has some disadvantages such as insufficient surface hardness, low strength and brittle (Alhared et al., 2016).

2.3.2 (b) Types of fillers

Different fillers will have different influence toward the properties of the PMMA composites. Those reinforcements can be in polymer, metal and ceramic base materials. For polymer base fillers, they consist of polyethylene fibre and vegetable fibre. For metal base fillers, they can be silver, stainless steel, aluminium and copper. Ceramic materials such as glass fibre, carbon fibre, silica, zirconia, alumina and barium titanium oxide also suitable in reinforcing PMMA resin.

i. Polyethylene

Polyethylene is a naturally crystalline polymer which is drawn at temperature below its melting point. This method is to produce polymer with enhanced modulus in the axial direction. Polyethylene exhibits many favourable properties to be used as reinforcement agent in PMMA which consists of high ductility, neutral colour, low density and superior biocompatibility. Polyethylene can be drawn as monofilament fibres and woven fibres. Other than that, in order to improve the adhesion between PMMA and polyethylene, electrical plasma treatment can be used to treat the surface of polyethylene. This treatment is to etch the surface of fibre into which the resin gets impregnated, so that it can bond mechanically to the resin phase (Rama, 2013). The fibres concentration, orientation and length are also greatly influence the mechanical properties of polyethylene fibre reinforced PMMA resins. Based on Gutteridge (1992) research, polyethylene fibres treated with electrical plasma treatment and less than 3 wt%, they found the significant improvement in the strength. Then further research had been done and found that the concentration of polyethylene as low as 1 wt% can significantly improve the impact strength of PMMA composite. However, if the concentration of polyethylene is over 3 wt%, it will make the dough un-work. Uzun et al. (1999) repored that woven polyethylene fibres reinforcement can significantly increase the impact strength and elastic modulus. Mallikarjuna et al. (2015) stated that polyethylene fibres in weave form exhibited better strength compared with metal base reinforcement due to polyethylene fibres are ductile and not brittle and have high modulus of elasticity.

ii. Vegetable fibre (Ramie fibre)

Vegetable fibre is one of the promising biomaterials due to its biocompatibility properties. Due to Ramie fibre occupies higher Young's modulus and ultimate tensile strength than denture base resin, so it has the potential as reinforcing agents for denture base. Ramie is one of the oldest textile fibres which known as "china grass", these are referred as bast fibres and come from the phloem tissue of plant (Jie Xu et al., 2013). Moreover, its whiteness might also fulfil the requirement of denture base aesthetical appearance. Based on previous work by Jie Xu et al. (2013), there were two crucial influence factors being studied to claim the effect of ramie fibres toward PMMA resins in flexural properties of composite which were fibres volume fraction and fibres length. From the result obtain with 10 vol% of 1.5mm fibres addition, the flexural modulus of denture base PMMA rose from 2.5 GPa to 3.46GPa, while the flexural strength of composite declined steadily with the increase of fibres contain. For 3.0 mm fibres, the modulus showed a growth from 2.5 GPa to 3.5GPa at 4 vol% of filler then dropped back to 3.00GPa at 10 vol%, whereas fluctuation in strength was experienced.

iii. Metal fillers

The function of metal filler in acrylic denture base materials is to improve the mechanical strength of composites. Metal fillers had been focused in research for some period. Those metals include silver, stainless steel, aluminium and copper filler. The purpose of added metal fillers was to improve the compressive strength, thermal conductivity, decrease the curing shrinkage and water sorption of PMMA composite (Sehajpal & Sood, 1989). However due to the drawback of lacking interfacial bonding between metallic fillers and the PMMA resin, the addition of metallic fillers is considered not successful (Gutteridge, 1992).

From the early research from Sehajpal (1989), metallic filler of silver, aluminium and copper at 25% concentration able to increase the thermal conductivity of PMMA by 4.53, 4.43, 4.04 times compared to unreinforced PMMA resins. Besides the compressive strength of PMMA composites was increased with the addition of metal fillers, but the tensile strength was decreased (Sehajpal & Sood, 1989). Base on the research of Mallikarhuna (2015), stainless steel show the lowest impact strength compare to glass fibre and polyethylene fibres due to stainless steel lack of interfacial bonding with PMMA resins. Other than that, based on Beyari (2015), silver filler used as reinforcement of PMMA resin showed the lowest amount of water sorption which is around 0.39mg/cm^3 compared to unreinforced resin which is around 0.42mg.cm^3 (Beyari, 2015).

iv. Zirconia

ZrO_2 has variety of advantage properties which consists of excellent toughness, mechanical strength, resistance to physical corrosion, abrasion resistance and biocompatibility (Mallineni et al., 2013). Zirconia had been applied as clinical materials, especially for denture and artificial bone production and reparation (Damestani et al., 2013). Based on the research by Wei Yu et al. (2014), which used ZrO_2 nanotubes and nanoparticles as the reinforcing agent for PMMA resins, 2 wt% of untreated ZrO_2 nanotubes showed the highest reinforcement effect in bending stress and bending displacement compared with various of additive content of treated ZrO_2 nanotubes, treated ZrO_2 nanoparticles and untreated ZrO_2 nanoparticles. This is because ZrO_2 nanotubes had unique long tubular structures. Hence, when mixed with PMMA the polymer chains wound around the added nanotubes and formed a three-dimensional network structure without any bonding effect. These let the polymer chain could slip along the nanotubes axis under an external force (Wei Yu et al., 2014). In addition, PMMA incorporate with 2 wt% of ZrO_2 able to increase their impact strength up to 6.55 KJ/m^2 (Asar et al., 2013). While the additional of ZrO_2 filler up to 20 wt%, it will decrease the impact strength and hardness of PMMA composite compare to PMMA control group (Asopa et al., 2015).

v. Glass fibres

Glass fibres were tested as reinforcement for denture base PMMA since 1960s (Vallittu, 1996). They had been used in different forms to enhance dental polymers which include woven, loose, short-rod and continuous fibres. The reasons glass fibres were suitable to be used as reinforcing agent for denture base materials because they had excellent aesthetic appearance, superior mechanical properties and biological compatibility. Although glass fibres are not very resistant to impact forces, but it can be improved by using unidirectional or woven glass fibres (Goguta et al., 2006). However, due to the deleterious effect on the doughing properties, the incorporation of glass fibres was limited to 20 wt% (Jagger, 1999). In addition, to improve the mechanical properties of glass fibre in reinforced PMMA, strong adhesion bond between glass fibres and PMMA matrix is very important. Hence glass fibres will treat with silane coupling agent before loading into the PMMA resins.

There were several research had been carried in pass few years regarding glass fibres as reinforcement in composites. For example, Unalan et al. (2010) had reported that the transverse strength is higher with woven fibre reinforcement than the unidirectional glass fibre reinforcement. Besides, Yondem et al. (2011) have observed less flexural strength with glass fibres compared to carbon and aramid fibres reinforced along the long axis of the specimens. Under Beyari (2015) research, by adding 0.16gm weight of glass fibres, it shows a significant dimensional accuracy. Figure 2.2 show the result reported by Beyari.

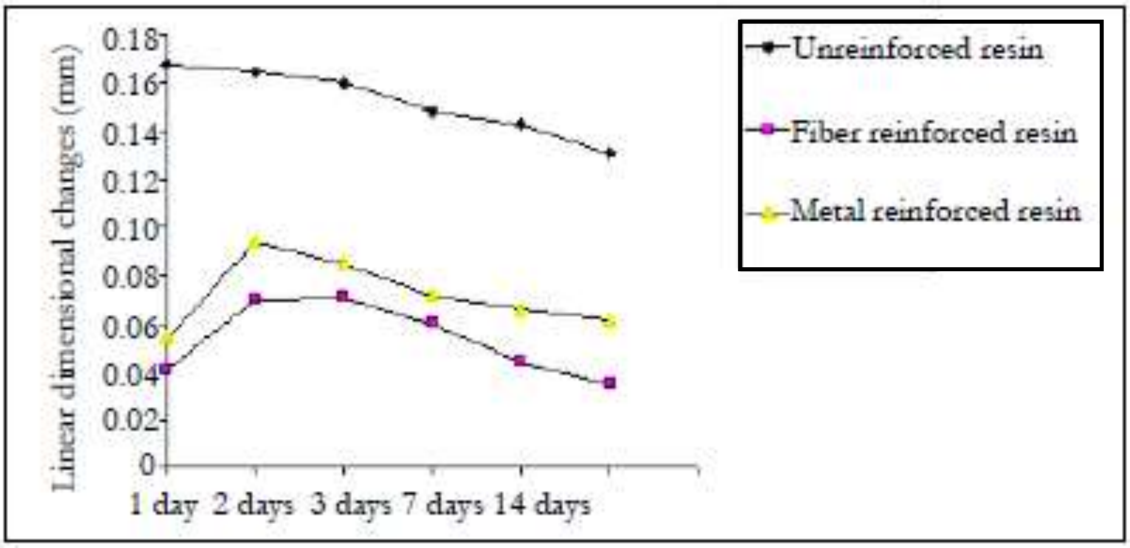

Figure 2.2: Mean linear dimensions (mm) of the test specimens after processing 1-day, 2-days, 3-days, 1-week and 2-weeks of storage in water (Beyari, 2015).

vi. Carbon Fibres

Carbon fibres were first made commercially by Edison in late 19th century by carbonizing thin bamboo shoots and carbon fibres. Carbon fibres were mainly used to improve fatigue behaviour and impact strength of the PMMA composite. However, carbon fibre is difficult to handle when it was dry, hence it must be wetted with monomer to form the town of wet fibre (Jagger et al., 1999). Besides, carbon fibres must be coated with a silane coupling agent to provide strong adhesion bond between carbon fibres and PMMA resins. Although carbon fibres provided significant improvement in mechanical properties of PMMA, but due to its cytotoxicity properties it was not suitable used in denture application. It was a possibility of skin irritation on handling carbon reinforced denture base specimens (Rama et al., 2013).

vii. Alumina (Al_2O_3)

Aluminium is one of the most cost effective and widely used material in the family of engineering ceramic. This is due to its positive properties which are excellent in size and shape capability, high strength, high stiffness and high availability. Besides, alumina was suitable used as reinforcing agent. This is because, alumina is stiffer and more brittle than PMMA resins, therefore it is suitable improve the properties of dental composite (Alsharif et al., 2014). Nevertheless, numerous researches had been carried by using alumina as reinforcing agent. For examples, Zhang et al. (2015) had studied the effect of particles size and contents on the thermal conductivity and mechanical properties of alumina with high density polyethylene (HDPE) composites. In their study, smaller particles size show better performance. Moreover, composite filled with 0.5 μm Al_2O_3 at 25 vol% show the best synthetic properties. Besides Alhareb et al. (2011) had studied the effect of Al_2O_3/ZrO_2 reinforcement on the mechanical properties and osteoconductivity. Alhareb et al. (2015) continued study on the mechanical properties of Al_2O_3/ZrO_2 with PMMA resins, but in this research, they applied nitrile butadiene rubber (NBR) as impact modifier. The addition of NBR particles into composite could be useful in absorbed a portion of fraction or impact strength and transfer the composite from brittle to ductile characteristic. Besides, there were some improvement in 2016 regarding the same research field (Alhareb et al., 2016).

viii. Hydroxyapatite

Hydroxyapatite (HA) is an amorphous calcium phosphate which has calcium: phosphorus (C: P) ratio of 10: 6 with chemical formula $Ca_{10}(PO_4)_6(OH)_2$, was introduced in year 1975 as filling material for intrabody defects. Besides, HA is considered as bioactive filler because of its similarity toward the biological HA in impure calcium phosphate form which founded in human bone and teeth. It is attractive biomedical material owing with its excellent biocompatibility, osteo-conductivity, osteophilic and non-toxicity chemical components (Kantharia et al., 2014).

Synthetic HA has almost similar composition to the mineral component which exist in bone and teeth of human. This is the reason why most of the clinic tend to use HA as biomaterial for medical and dental application (Dorozhkin and Epple, 2002). The detail of the composition of HA is showed in Table 2.1. In addition, compare to other reinforcing agent, hydroxyapatite consist has low mechanical strength and fracture toughness. Table 2.2 shows the typical properties of dense hydroxyapatite.

Table 2.1: Chemical comparison between bone, teeth and hydroxyapatite (HA) (Al-Sanabani et al., 2013).

Composition, wt%	Enamel	Dentine	Bone	HA
Calcium	36.5	35.1	34.8	39.6
Phosphorous	17.1	16.9	15.2	18.5
Ca/P ratio	1.63	1.61	1.71	1.67
Total inorganic (%)	97	70	65	100
Total organic (%)	1.5	20	25	—
Water (%)	1.5	10	10	—

Table 2.2: Typical properties of dense hydroxyapatite (Al-Sanabani et al., 2013)

Properties	Amount
Theoretical density	3.156 g/cm^3
Hardness	500–800 Vickers, 2000–3500 Knoop
Tensile strength	40–100 MPa
Bend strength	20–80 MPa
Compressive strength	100–900 MPa
Fracture toughness	1 $MPam^{1/2}$
Young's modulus	70–120 GPa

There were a lot of researches had been done on HA as reinforcing agent for bone cement and denture base agent. In year 2010, Tham and his group made a research on the effect of treated PMMA/HA composite toward the mechanical, thermal and morphological properties. In this experiment, different percentage of surface treatment agent were used and its maximum performance toward mechanical and thermal properties were observed. Zebarjad et al. (2011) reported on the mechanical properties of PMMA with HA nanocomposite to observe the compressive strength, yield strength and modulus of composite with different composition. In same year, Hamizah et al. (2011), areported on the mechanical and thermal properties of PMMA bone cement reinforced with various weight precentage of HA and glass ceramic fillers. Hongquan et al. (2012) published two articles on the failure behaviour and mechanical properties of HA whisker-reinforced bis-GMA-based resin composites. They used various filler loading to find the optimum filler required to get maximum properties. Calabrese et al. (2016) compared between HA whiskers based resin composite with commercial dental composites in mechanical properties ad bio-compatibility characterization.

ix. Tricalcium Phosphate (TCP)

Tricalcium phosphate had been researched since early 1970s. It is existing in many different polymorphs which consists of α, β, γ, and super-α (Gibson et al., 1996). However, there are just two polymorphs phase which are α, β phases are used as biomaterials (LeGeros, 2002). Although, β-TCP extensive research since early 1970s, but it is still lack of clarity concerning about this material.

TCP mostly behave as osteo-conductive materials which permits bone growth on their surface or into pores, channels and pipes. Other than that, it is also a biocompatible material which useful in inducing hard tissue formation and support the bone growth.

Although there are a lot of advantages for TCP, but it still has some drawbacks which consist of difficult to sinter, difficult to fabricate, low mechanical strength and low resistance to crack-growth propagation (Al-Sanabani et al., 2013).

There were few researches had been carried within in this two years regarding TCP used in different application. Munoz-Corcuera et al. (2015), investigated on the post extraction application of β-TCP on alveolar socket (Munoz-Corcuera et al., 2015). Shu-Hsien et al. (2016) studied on the fabrication and characteristic of polycaprolactone and β-TCP composites for tissue engineering application. In same year, Sachiko et al. (2016), reported on the effect of β-TCP particles on primary cultured murine dendritic and macrophages. Rupita and Ritwik (2016), also investigated on the synthesis and characterization of sintered β-TCP which made a comparative study on the effect of preparation route.

x. Polylactic acid microsphere

Polylactic acid (PLA) is an aliphatic polyester which has outstanding advantage compared to other polymers. In early 1970's, PLA products have been approved by U.S Food and Drug Administration (FDA) for direct contact with biological fluids. Hence PLA are safe to be use for oral application. PLA and its degradation products, H2O and CO_2 are not toxic and carcinogenic to human body. With this properties, PLA is used in biomedical application which include sutures, clips and drug delivery system (DDS) (Lin et al., 2012). Microspheres are small spherical particles which in micrometer range. Microspheres sometimes referred to as microparticles. Hollow microsphere are widely in density, hence it able use in different application. Among those polymer microsphere, PLA is one of the polymer which safety has been evaluated completely and being approved by FDA (Analava and Baishakhi, 2011).

2.4 Nitrile Butadiene Rubber (NBR)

Nitrile is one of the most commonly used elastomer in seal industry. Besides, it is copolymer between two monomers which are acrylonitrile (ACN) and butadiene. The properties of these nitrile rubber compounds are determined by its acrylonitrile content, which can divide in three stages: ACN content more than 45% consider high, ACN content between 30-45% consider medium while low mean ACN content less than 30%. The higher the ACN content, the better the resistance to hydrocarbon oils. The lower the ACN content the better the flexibility of nitrile rubber compounds in low temperature application (Eriks, 2017). Nitrile butadiene rubber (NBR) has various of advantages which make it suitable used in denture base material as modifier. For example, NBR shows no allergic reaction when contact with oral tissue of prosthesis and it consists as non-toxic material. In addition, it acts as impact modifier in PMMA resins to improve its impact strength (Alhared et al., 2015). Only few researches considered adding NBR in denture base material to manipulate its mechanical properties. Alhareb and his team studied on Al_2O_3/YSZ filler reinforced PMMA resin with modify by adding NBR in years 2015 and 2016 (Alhareb et al., 2015; Alhareb et al., 2016).

2.5 Fabrication of PMMA Composite.

2.5.1 Mixing Process

Different polymer composite will have different ways or sequences in fabrication process. Difference ways or sequences in fabricate polymer composites will have their own parameter and condition required. Hence, suitable mixing process for the product is the prerequisite in success a composite. Then, followed by subsequent processes such as molding, curing and surface finishing. All these steps need to be considered, because every step will influence the final performance of the composite product.

There are several compounding methods can be used in produce composite products such as mixer, extruder, mills and hand stirred. Table 2.3 shows some of the compounding methods which can be used in polymer composites.

Table 2.3: Types of primary compounding machinery with its advantages and disadvantages (Robert, 2013).

Types of Mixer	Advantages	Disadvantages
Batch Mixers	Accepts all feed forms High output Good for short production runs Long life expectancy Can automated Broad range of shear capability	Varying power demand Batch to batch variation Post mixer variable product heat history Capital intensive Need post mixer forming Can be labour intensive
Continuous Mixers	High output Energy efficient Ease of process optimization Easily automated Uniform product shear and heat history	Require free flowing feed Require sophisticated weigh and feed systems Not applicable for short runs Difficult to clean Capital intensive Need post mixer forming
Twin Screw Extruders	Energy efficient Ease of process optimization Easily automated Geometry optimized for use Uniform product shear and heat history	Require free flowing feed Require sophisticated weigh and feed systems Not applicable for short runs Difficult to clean Capital intensive Configuration changes required

Table 2.3: Types of primary compounding machinery with its advantages and disadvantages (Robert, 2013).

Mills	Very versatile Broad range of shear capability Accepts all feed forms Good for short production runs	Difficult to control Difficult to automate Batch to batch variation Dirty operation Safety considerations Low output Varying power demand Labour intensive

a. Internal mixer

Internal mixer basically was developed by Banbury and pioneered by the new Farrel Corp. For modern internal mixer, it consists of mixing chamber with two counter rotating rotors. In addition, it is preferable in laboratory study which due to the homogeneity of product after mixing process. These will directly enhance the overall properties of the composites. Moreover, internal mixer can be automated and able to accept all the feed form raw materials. Figure 2.3 shows the structure of internal mixer. Alhareb et al. (2015) compounded PMMA with Al_2O_3/YTZ filler and NBR in internal mixer (599957-K model, MS Instruments, Malaysia) at rotor speed 50 rpm and heated at 65˚C.

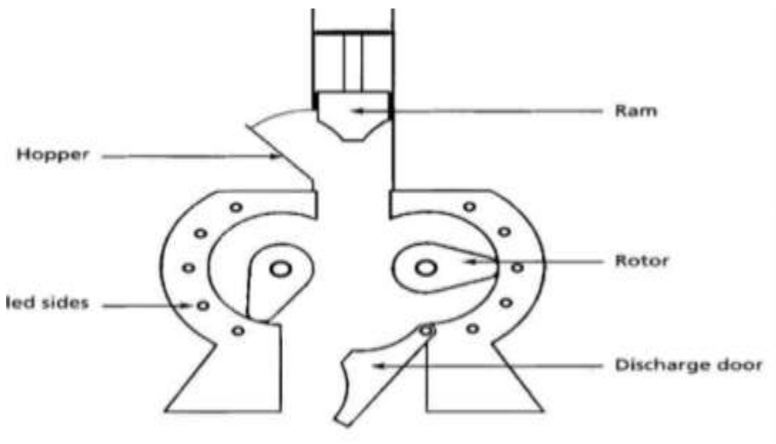

Figure 2.3: Conceptual cross-section through an internal mixing machine (Bajwa, 2014).

b. Vacuum Mixer

There are several vacuum mixers being used in compounding composites. Vacuum mixer is piece of equipment that allow mix the compounds in vacuum condition to limit the excess of air in the mixer and prevent the formation of bubble in the compound. Vacuum mixer includes a central mixer drum with blade insert, designed to be fitted inside a casing to pump out air and create vacuum condition. The level of vacuum and pressure can be adjustable depend to the application. Hamizah et al. (2011) used Stryker Mixevac III bowl connected to vacuum pump to mix bone cement with glass filler and HA. Yingying et al. (2012) mixed their samples in vacuum condition at 60˚C for 30 minutes. While Al-Bakri et al. (2014) dispersed their mixtures in vacuum mixer for 5 minutes to ensure not bubble inside the compounds.

c. Twin Screw Extrusion

The twin screw extrusion process enables the continuous production of highly homogeneous and finely structured products by using bio-sourced or synthetic raw materials. The aims of extrusion process are to physico-chemically transform continuously viscous polymeric media and produce high quality structure product. The benefits of twin screw extrusion are remarkable mixing capability, high level of process flexibility, better control of process parameters, higher process productivity and higher economic opportunities and business potential. Jyh-Horng et al. (2015), fabricated PLA/PMMA/SiO2 composites by mixing PLA and PMMA with stearic-acid-modified nano-silica with twin-screw extruder (Nanking Jia-Ya SHJ-20, China) at 200˚C to allow the components to mix efficiently.