The Influence of Chicken Egg Shell as Fillers on Biocomposite Acrylic Resin for Denture Based

M Lubis1*, M H S Ginting1, N F Dalimunthe1, D M T Hasibuan1, and S Sastrodihardjo2
1Department of Chemical Engineering, Faculty of Engineering University of Sumatera Utara, Jl. Almamater Kampus USU Medan 20155
2Faculty of Dentistry, University of Sumatera Utara, Jl. Almamater Kampus USU Medan 20155

*maulida70@gmail.com

Abstract. This research was conducted to discover the influence of the addition of chicken egg shells microparticle as filler on the mechanical properties such as modulus of elasticity, modulus of rapture and particle size analysis on biocomposite acrylic resin for denture based. The raw materials used in this research were acrylic resin, egg shell, cold mold seals, gypsum, Vaseline and wax. The process of making biocomposite acrylic resin for denture based with mix the acrylic resin in ratio 2:1 (w/w). Then added the microparticle filler 0,10,20,30 (%w) to mold and boil in 75 ºC for 90 minutes and increase the temperature to 90 ºC for 30 minutes. Took the sample and let it dried. The results of research showed the increase of modulus elasticity and modulus of rapture. The modulus of elasticity showed a very significant increase by adding fillers 10% of 2.123 GPa, which was only 1.932 GPa without adding the filler of chicken egg shells. For modulus of rapture showed the increase by adding fillers 20% of 48,311MPa, which was only 46,865 GPa without adding the filler of chicken egg shells.

1. Introduction
According from Department of Health of the Republic Indonesia (RISKEDAS) that tooth loss of Indonesia population has increased every year [1]. With the increasing number of tooth loss of Indonesia’s population, the use of denture base will be increase too.

The denture base is that part of the denture which rests on the soft tissues and so does not include the artificial teeth [2]. The denture base materials must be biocompatible and should have a good aesthetic appearance [3]. Non metal denture base usually made of a polymer material which is until become the first choice [4][5]. Acrylic resin is a polymer which is most widely used in dentistry because it has good optical properties and a small solubility in body fluids [6].

Most of acrylic resin added with some fibers filler, such as carbon fiber, glass fiber, and polyethylene fiber [7]. Shortages of some types of fiber filler are difficult to absorb resin monomer, so it can make a gap between the surface of the fiber with the polymer matrix, and reducing the mechanical strength of
the resin \cite{8}. The mechanical properties of the composite material is influenced by the shape, size and distribution of filler particle in the matrix \cite{9}.

Chicken egg shells have been used as a power source for calcium \cite{10}. Chicken egg shells containing calcium and other micro elements, such as magnesium, boron, copper, iron, manganese, sulfur and zinc. The high content of CaCO$_3$ (Table 1) making the egg shells as a commodity that has potential as starting material biocompatible biomaterial \cite{11,12}. We can see the composition of chicken egg shells from table 1. Another advantages of chicken egg shells are cheap and abundant amount \cite{13}.

| Nutrition   | Contents (% W) | Nutrition   | Contents (% W) | Nutrition   | Contents (% W) |
|-------------|----------------|-------------|----------------|-------------|----------------|
| Water       | 29 - 35        | Sulphur     | 0,09 - 0,19    | Leucine     | 0,57           |
| Protein     | 1,4 - 4        | Alanine     | 0,45           | Lysine      | 0,37           |
| Crude fat   | 0,1 - 0,2      | Arginine    | 0,56 - 0,57    | Methionine  | 0,28 - 0,29    |
| Ash         | 89,9 - 91,1    | Aspartic acid| 0,83 - 0,87    | Phenylation| 0,38 - 0,46    |
| Calcium     | 35,1 - 36,4    | Cystine     | 0,37 - 0,41    | Proline     | 0,54 - 0,62    |
| CaCO$_3$    | 90,9           | Glutamic acid| 1,22 - 1,26    | Serine      | 0,64 - 0,65    |
| Phosphorus  | 0,12           | Glycine     | 0,48 - 0,51    | Thereonine  | 0,45 - 0,47    |
| Magnesium   | 0,37 - 0,40    | Histidine   | 0,25 - 0,30    | Tyrosine    | 0,25 - 0,26    |
| Potassium   | 0,10 - 0,13    | Isoleucine  | 0,34           | Valine      | 0,54 - 0,55    |

Chicken egg shells fillers are expected to be used as an alternative filler material in the manufacture of denture base. In addition the use of chicken egg shells as a filler can reduce the cost of installation in the denture base and can produce the environmental friendly products.

2. Method

2.1. Chicken Egg shells Filler Preparation

Chicken egg shells washed, then dried in an oven at 60°C for 60 minutes, delicate the chicken egg shells in a ball mill for 5 hours and analyzed by particle size analysis (PSA) to obtain microparticle chicken egg shell \cite{14}. The result of the analysis shows a particle size of 100,032 µm.

2.2. Mold Preparation

To make a mold, 30 g gypsum mixed with 250 ml of aquadest. Pour the gypsum dough on the bottom cuvet then put the wax pattern (ISO 178-2001). Give vaseline on the surface of the hardened gypsum. The top cuvet filled with gypsum that have a same comparison with the bottom cuvet. Top and bottom cuvet make become together and press for 90 minutes. Take out the wax pattern on the mold and then gypsum surface smeared with CMS and left for 20 minutes \cite{4}.

2.3. Experimental of Biocomposite Danture Base

Denture base materials are mixed with a ratio of 2:1 (w:w), until the liquid is absorbed by the powder then add the fillers and stir until the dough phase stages. Pour the dough into a mold then put the top and bottom cuvet together in the press. Open the cuvet to clean the dough out. Put the top and bottom cuvet together and locked with a bolt \cite{4}.

Cuvet boiled in a water bath at 75°C for 90 minutes after 90 minutes raised the temperature to 100°C for 30 minutes. Pick up the cuvet and allowed to cool at room temperature. Open the cuvet and then take out the sample of denture base from mold \cite{4}.
Samples of biocomposite were tested to see the mechanical properties. Tests carried out is the modulus of elasticity (MOE) and modulus of rapture (MOR). Then characterized with Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR).

3. Results and Discussions

3.1. Characterization of Particle Size Analysis (PSA)
Characterization of particle size analysis (PSA) was conducted to determine the particle size of chicken egg shells filler that obtained from this study. Fig. 1 shows the result for the characterization of particle size analysis (PSA).

![Figure 1. Characterization of Particle Size Analysis (PSA)](image)

Figure 1 shows a comparison of the particle concentration with the particle size that are obtained. From fig. 1, we can see that the size obtained in the range 90-100 µm, which 90% is the concentration of particle size 100,03 µm.

3.2. Characterization Fourier Transform Infrared (FTIR)
Characterization Fourier Transform Infrared (FTIR) of chicken egg shells, denture base matrix and biocomposite denture base sample which is have a microparticle filler chicken egg shells can be seen in the following fig. 2

![Figure 2. Characterization Fourier Transform Infrared (FTIR) of chicken egg shells, denture base matrix and biocomposite denture base of chicken egg shells microparticle filler](image)
From figure 2 we can see a decreasing in absorption peak wave number at 3437 cm\(^{-1}\) which is a stretch of alcohol (OH). Discontinuation of carbon cluster from alkane (CH) at wave number 2947 cm\(^{-1}\) shows the alkane group (CH) on the denture base has bonded with filler chicken egg shells. There was a decrease absorption peaks at wave lengths 2515 for egg shells, which is stretch of sulfur (SH), but in biocomposite of denture base that has a filler of chicken egg shells, not found anymore sulfur content. Furthermore detected aldehyde group (\(>\text{CO}\)) in the biocomposite, it can be seen from a decreasing peaks and valleys formed at wave number 1728 cm\(^{-1}\) which is the stretch of the aldehyde (\(>\text{CO}\)). The group of nitrogen compounds (NO2) also detected at wave number 1446 cm\(^{-1}\) and alkyl halide (C-F) detected at wave number 756, 10 cm\(^{-1}\). From fig. 2 we can see that there’s no reactions occurs between the filler egg shells with acrylic resin matrix. It is strongly suggested with no new cluster appear in the denture base. But, the sulfur cluster that was detected in chicken egg shells not found in biocomposites. It is because of the sulfur turns into gas phase at a temperature of 95.5°C.

3.3. Effect Of Addition Microparticle Chicken Egg Shells Filler to Modulus of Elasticity (MOE) Biocomposite Denture Base

Modulus of elasticity (MOE) is a material’s ability to withstand deformation up to the limit of the proportion of material which exhibits elasticity. The higher MOE is, the more elastic the material.

![Figure 3. Effect of Addition Microparticle Chicken Egg Shells Filler to Modulus of Elasticity (MOE) Biocomposite Denture Base](image)

From figure 3 can be seen the effect of the composition of the filler to the modulus of elasticity (MOE) denture base. The MOE values obtained without the addition of fillers is 1.933 GPa; 2.124 GPa for the addition of 10% fillers; 2.118 GPa for the addition of 20% fillers and 1.474 GPa for the addition of 30% fillers. The value of the MOE on the addition of 10% and 20% fillers better than without addition of fillers. This is because of the load transfer between the filler with the matrix as a result of adhesion. The elasticity of denture base influenced by permanent deformation due to MOE of denture base is already above the threshold stress point. The addition of filler causes the increasing of threshold stress point from denture base since fillers absorb some of the load that received by the denture base, so it can increase the MOE of denture base\([8]\).

The best value of MOE obtained with the addition of 10% fillers and then the value of MOE decrease as the composition of the filler as increase. This is caused by the increasing of filler, while the number of matrix was decrease, so it cause a narrow area between phases where the filler is not evenly distributed in the matrix which cause the formation of empty fraction in the structure of denture base\([15]\).
3.4. Effect Of Addition Microparticle Chicken Egg Shells Filler to Modulus of Rapture (MOR) Biocomposite Denture Base

Modulus of Rapture (MOR) or fracture constancy is a mechanical properties of a material that indicates the maximum resistance of material which is acceptable until the material damaged or broken.

From figure 4 shows the effect of the composition of the filler to the modulus of rapture (MOR) denture base. The MOR values obtained without the addition of fillers is 46.864 MPa; 44.552 MPa for the addition of 10% fillers; 48.311 MPa for the addition of 20% fillers and 30.651 MPa for the addition of 30% fillers.

From fig. 4, we can see that the composition of filler of chicken egg shells affect the value of MOR, where fluctuations occurs in the results. The best value of MOR obtained on the addition of 20% fillers, but the value of MOR for the addition of 10% and 30% fillers were smaller than without the addition of fillers. It is caused by the effect of nitrogen group (NO2) were detected in the biocomposite. Nitrogen group can inhibit the distribution of the particles and cause small bubbles (voids) in the sample of biocomposite, it makes the resistance of denture base to fracture was decreasing. The various content of nitrogen in chicken egg shells causes the fluctuations in value of MOR. The best result for MOR were obtained for the addition of 20% fillers. That is because the addition of 20% fillers is the most ideal, resulting in a homogeneous mixture with a wide interphase, so the fillers can be distributed evenly and reduce the incidence of empty cavity on the biocomposite.

3.5. Characterization of Scanning Electron Microscope (SEM)

Characterization of Scanning Electron Microscope (SEM) was conducted to see the morphology of biocomposite denture base. The results of characterization can be seen in the following figure 5.
Biocomposite denture base - 10% chicken egg shells with 1000x enlargement.

Biocomposite denture base - 30% chicken egg shells with 1000x enlargement.

From figure 5 (a) can be seen the morphology of fracture from biocomposite denture base that has chicken egg shells filler with a concentration of 10%, has a smooth fracture surface but raggy and shown the particle pull out. While fig. 5 (b) shows the morphology of biocomposite denture base that has chicken egg shells filler with a concentration of 30%, has a rough and raggy fracture surface structure, so many voids are formed and so many concentration of particles in the matrix. From the characterization of scanning electron microscope (SEM) can be seen the addition of 10% fillers obtained that the distribution of particles more evenly than the addition of 30% fillers that has a minimum regional interphase because the concentration of filler is too much, so it causes accumulation of filler particle which effects in the uneven distribution of filler particle.

4. Conclusions
The addition of chicken egg shells filler in the acrylic resin for denture base obtains a biocompatible material. It can be prove from the increasing of mechanical properties of biocomposite denture base. Modulus of Elasticity (MOE) and Modulus of Rapture (MOR) of biocomposite was increasing with the addition of chicken egg shells.

5. Acknowledgments
The authors gratefully acknowledge that the present research is supported by Ministry of Research and Technology and Higher Education Republic of Indonesia. The support is under the research grant BP-PTN USU of Year 2016 Contract Number 6049/UN5.1.R/PPM/2016.

References
[1] Sugianitri N K 2011 Ekstrak Biji Buah Pinang (Areca Catechu L.) Dapat Menghambat Pertumbuhan Koloni Candida Albicans Secara In Vitro Pada Resin Akrilik Heat Cured (Denpasar: University Udayana)
[2] McCabe J F and Walls A W G, 2008 Applied Dental material 9th ed (Oxford: Blackwell).
[3] Thomas R M and Mark A L 2005 Physical Properties of Four Acrylic Denture Base Resins J. Dent. Practice 6(4):93-100.
[4] Wennie F 2013 Perbedaan Pengaruh Penambahan Serat Kaca dan Serat Poliester terhadap Kekuatan Impak Bahan Basis Gigi Tiruan Resin Akrilik Polimerisasi Panas (Medan: University of Sumatera Utara).
[5] Muskab 2012 Pengaruh Larutan Tablet Pembersih Gigi Tiruan Terhadap Kekuatan Transversa Lempeng Akrilik (Makassar : University Hassanudin).
[6] Raszewski Z and Nowakowska D Mechanical Properties of Hot Curing Acrylic Resin After Reinforced With Different Kinds of Fibers Int J. Bio. Mater. Res. 2013;1(1):9-13.
[7] Beyari, M.M., et al. Effect of Glass Fibers or Metallic Filler On The Linear Dimensional Changes and Water Sorption Of Acrylic Resin Denture Base Material. (2015) J Dent & Oral Care 1(4): 1-4
[8] Ferasima R, M Zulkarnain, and Hubban Nasution 2012 The Effect Of Glass Fiber And Polyethylene Fiber Addition On Impact And Transverse Strength Of Denture Base Material Heat Polymerized Acrylic Resin (Medan: University of Sumatera Utara)
[9] D. Chauhan, N Singhvi and R. Singh, Effect of Geometry Of Filler Particles On The Effective Thermal Conductivity Of Two-Phase Systems. Int. J. of Modern Nonlinear Theory and Application. Vol. 1 No. 2, 2012, pp. 40-46.
[10] Hunton P. (2005) Research on Egshell Structure and Quality: An Historical Overview. Brazilian Journal on Poultry Science, 7, 67-71.
[11] A.M. King’Ori. A Review of The Uses of Poultry Eggshells and Shell Membranes. Int. J. of
Poultry Science. 10 (6): 483-492, 2011.
[12] Amrina, Q H (2008) Sintesa Hidroksiapatit Dengan Memanfaatkan Limbah Cangkang Telur:
Karacterisasi Difraksi Sinar-X dan Scanning Electron Microscopy (SEM) (Bogor: Institut
Pertanian Bogor).
[13] S Sanmuang, Y Ruksakulpiwat, N Suppakarn, and W Sutapun Chicken Eggshell as a Filler for
Polymer Composites: Preparation and Characterizations. Advanced Materials Research Vols
47-50, pp. 490-493, 2008.
[14] Gadri A, Sasanti T D, Rachmat M and M I Iwo Formulasi Sediaan Tabir Surya dengan Bahan
Aktif Nanopartikel Cangkang Telur Ayam Broiler J. Maths & Sains. Vol. 17 No. 3, 2012 (Bandung: Institut Teknologi Bandung).
[15] Daulay, S A, F Wirathama and Halimatuddahliana Pengaruh Ukuran Partikel Dan Komposit
Terhadap Sifat Kekuatan Bentur Komposit Epoksi Berpengisi Serat Daun Nanas. J. Tech.
Chem. USU. Vol 3. No 3, 2014 (Medan: University of Sumatera Utara)