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# THE EFFECT OF ADDITION NANOPARTICLE CHICKEN EGGSHELL FILLERS ON BIOCOMPOSITE ACRYLIC RESIN FOR DENTURE BASE

MAULIDA LUBIS[1,*], MARA B. HARAHAP[2], M. H. S. GINTING[1], D. M. T. HASIBUAN[1], N. F. DALIMUNTHE[1]

[1]Department of Chemical Engineering, Faculty of Engineering
Universitas Sumatera Utara, Jalan Almamater, Medan, 20155, Indonesia,
[2]Department of Physics, Faculty of Mathematics and Science,
Universitas Negeri Medan, Medan, Indonesia
*Corresponding Author: maulida@usu.ac.id

**Abstract**

Chicken eggshell contains a high mineral compound, so it is suitable to use as nanoparticle filler. In this research, preparation of denture base with nanoparticle chicken eggshell filler and the variation of filler concentration was 0, 10, 20, 30 (% wt). Preparation of matrix acrylic denture base was processed by mixing powder of the acrylic resin and liquid monomer with the weight ratio 2:1, after that matrix is mould in a cuvette, then polymerized by boiling in water at 75°C for 90 minutes, after 90 minutes, temperature was raised to 100 °C and left for 30 minutes. Characterizations on denture base samples are included by MOE, MOR, FTIR, XRD and TEM. The best result is the addition with 10% filler, in which the modulus of elasticity test (MOE) shown the elasticity of sample are 2.571 GPa, and modulus of rupture test (MOR) shown the rupture of sample are 48.859 MPa.

Keywords: Biocomposite, Chicken eggshell, Denture base, Nanoparticle, Resin.

# 1. Introduction

Chicken eggshells have been used as an energy source for calcium [1]. Chicken eggshells contains calcium and other microelements, such as magnesium, boron, copper, iron, manganese, sulphur and zinc. Egg shells contain about 94% of $CaCO_3$, so it has the potential to be a biocompatible biomaterial [2, 3]. Chicken eggshells fillers are expected to be used as an alternative filler material in the manufacture of denture base. In addition the use of chicken eggshells as a filler can reduce the cost of installation in the denture base and can produce the environmentally friendly products. 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 suitable and biodegradable.

Acrylic resin is the most commonly used polymeric material in dentistry [4]. Poly methyl methacrylate (PMMA) acrylic resin has numerous advantages that make it the most frequently polymer used as denture base material [5]. Thermosetting machines has low viscosity and low molecular weight, so it is necessary to add suitable additives to improve the properties and strength of materials. [6]. Acrylic resins are derivatives of ethylene compounds containing vinyl groups in their structural formulas [7].

Nanoparticles are currently considered to be high potential fillers for the improvement of mechanical and physical properties of polymer composites. The width of the matrix-filler interface is high because uniform and homogeneous dispersions of the nanoparticles are responsible for altering the properties of flexibility, as well as mechanical properties, molecular mobility, and thermal properties. Nanoparticle filler, which has a larger aspect ratio (the largest ratio to the smallest dimension) suggests better reinforcement for nanoparticle composite production [8]. Sonication processing is by emulsifying and dispersing the material. Most of the sonication with high intensity is done using the method of cavitation sonication. Cavitation that occurs gives the effect of vibration that moves the material up and down with high pressure [9]. Chicken eggshell as filler in form nanoparticles is expected to provide good strength to denture base products and be environmentally friendly.

# 2. Materials and Methods

## 2.1. Nanoparticle chicken eggshells preparation

Chicken eggshell was crushed in a ball mill for 4 hours. Then sieved with 320 mesh sieves until the remaining particles was less than 100 micros. The sieved particles were suspended into Tween 80 solution with 1% solution concentration. Suspension of chicken eggshell grilled with high energy ball mill for 4 hours. Particles suspended by sonication method for 60 minutes using an ultrasonic bath instrument. Nanosuspension was inserted into the dialysis membrane and soaked in 100 ml of aqua, after that the aqua was evaporated at 100 °C to obtain the eggshell nanoparticles [10].

## 2.2. Mold preparation

To make a mold, 30 g of 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 [11].

## 2.3. Experimental of biocomposite denture base

Denture based 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. 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 cool it at room temperature. Open the cuvet and then take out the sample of denture base from mold [11].

## 2.4. Modulus of elasticity (MOE) and modulus of rapture (MOR)

Modulus of elasticity (MOE) and modulus of rupture (MOR) test of the sample was observed at Laboratory of Research, Department of Chemical Engineering, Universitas Sumatera Utara, Medan.

## 2.5. Fourier transform infrared (FTIR) and x-ray diffraction

Analyse of Fourier Transform Infrared (FTIR) using by Thermo Scientific Nicolet iS10 and X-Ray Diffraction (XRD) of the sample was observed using 6100 Shimadzu.

## 2.6. Transmission electron microscope (TEM)

Analysed Transmission Electron Microscope (TEM) of the sample was observed by JEM-1400 transmission electron microscopy.

# 3. Results and Discussion

## 3.1. Characterization transmission electron microscope (TEM) of nano-particle chicken eggshell

Characterization of Transmission Electron Microscope (TEM) to the eggshell nanoparticle filler was conducted to analyse the shape and size of eggshell nanoparticles. Figure 1 shows the results of characterization. The particles have an irregularly coarse grain shape with diameter ranges of ≤ 35 nanometres. Nanoparticles are defined as very small solid particles with less than 100 nm. These tiny particles with nanometre scales are the transition regions between the molecular scale and the macroscopic scale [12].

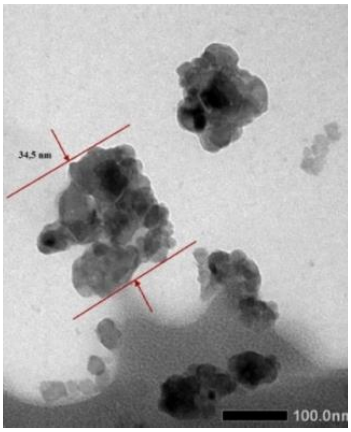



**Fig. 1. Characterization of transmission electron microscope (TEM) nanoparticle chicken eggshell with 100 nm enlargement.**

### 3.2. Characterization x-ray diffraction (XRD)

Characterization X-Ray Diffraction (XRD) to the eggshell nanoparticle filler was conducted to analyse the size of eggshell nanoparticles. Figure 2 shows the results of characterization.

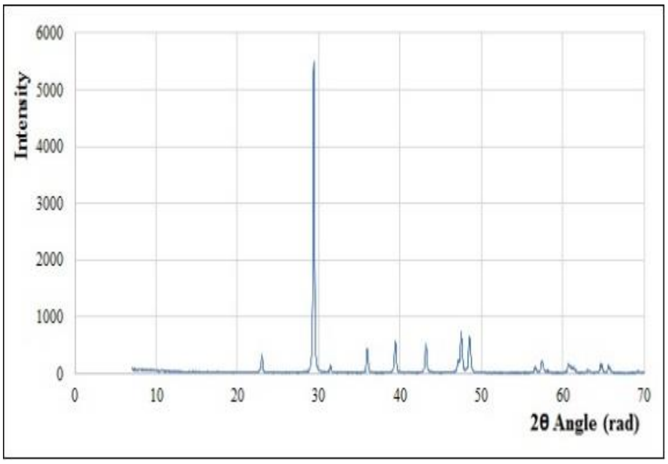



**Fig. 2. Characterization X-Ray diffraction (XRD) Nanoparticle chicken eggshell.**

The determination of the crystallization index of a material can be done by using the Seagal method, the principle of calculation is by dividing the intensity of the detected crystalline particles in the analysis by the total intensity of the crystalline and amorphous particles detected in percent on the XRD analysis. Figure 2 shows that the crystallization of the eggshell nanoparticle crystals obtained is 87.8%, indicated by the sharp peak of the spectra produced by the eggshell nanoparticle sample. The key absorption peaks of the spectra produced by eggshell nanoparticle samples were at $2\theta = 29.36°$; 47.48° and 48.49°. The absorption peak at $2\theta = 29.36$ ° which is the peak of the spectral absorption of crystalline nanoparticles of crystalline eggs, with the resulting particle diameter of 47 nm. Chinthakuntla et al. [13] obtained average particle size is 32 nm.

### 3.3. Characterization Fourier transform infrared (FTIR)

Figure 3 shows the characterization Fourier Transform Infrared (FTIR) of denture base matrix and biocomposite denture base sample with nanoparticle filler chicken eggshells.

The decrease of the absorption peak at the wave number 3437.15 $cm^{-1}$ preceded by vibration stretching indicates the presence of OH groups in aromatic alcohols (3200-3600 $cm^{-1}$ on O-H stretching). The absorption peaks occurring at the 1967.39 $cm^{-1}$ wave number indicate the presence of the C=O group of carbonyl compounds (1950-2050 $cm^{-1}$ referring to C=O stretching). The absorption peaks occurring at the wave number 1728.22 $cm^{-1}$ indicate the presence of the carbonyl group. At the absorption peak with the wave number 1442.75 $cm^{-1}$ indicating the presence of $NO_2$ groups of nitrite compounds (1300-1570 $cm^{-1}$ refers to -C-$NO_2$ stretching) [14, 15].

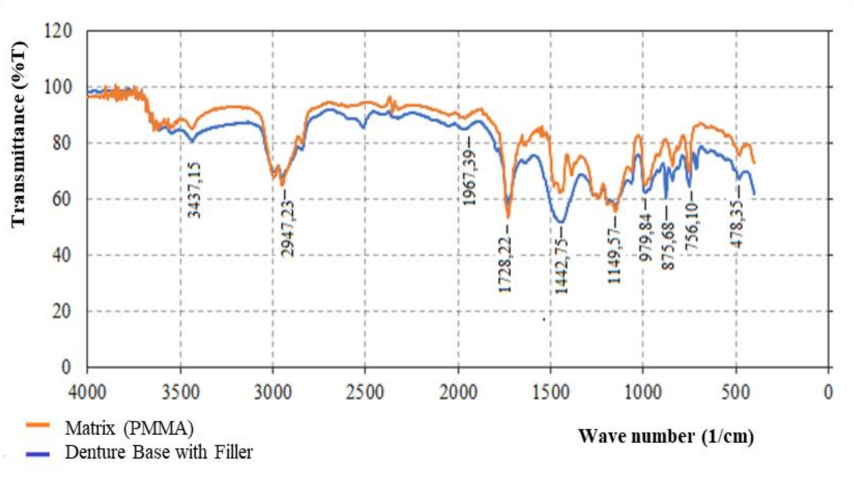
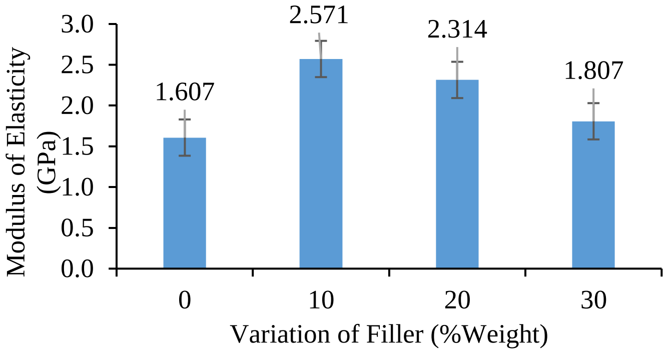



**Fig. 3. Characterization Fourier transform infrared (FTIR) of denture base matrix and biocomposite denture base of chicken eggshells nanoparticle filler shell.**

### 3.4. Effect of addition nanoparticle chicken eggshells 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 the value of MOE, the more elastic the material. The elasticity modulus test conducted in this study aims to determine the elasticity of the denture base. Figure 4 shows the effect of the filler concentration on the elastic denture base modulus. The elasticity modulus value obtained at the addition of 0% filler was 1.119 GPa; 10% of 2.571 GPa; 20% of 2.314 GPa; And 30% of 1.807 GPa.




**Fig, 4 Effect of addition nanoparticle chicken eggshells filler to modulus of elasticity (MOE) biocomposite denture base.**

Addition of the filler leads to an increase in mechanical properties [16]. The interfacial interaction between the nanofiller and matrix is influence on mechanical performance. The presence of a nano sized filler interacts with a composite matrix in order to reduce the deformation of the polymer molecule chain in the composite, resulting in the stretching occurring in the test performed to be reduced by the burden inherent in the filler [17]. Small particle size of the filler increases the degree of polymer strengthening versus large particle size. The particle size has a direct relationship with the surface area per gram of filler. Therefore, small particle size provides a large surface area for the interaction between the matrix polymer and the subsequent filler increases the strengthening of the polymeric material. In summary, the smaller the particle size the higher the interaction between the filler and the polymer matrix [18].

### 3.5. Effect of addition nanoparticle chicken eggshells filler to modulus of rapture (MOR) biocomposite denture base

Modulus of Rapture (MOR) or fracture constancy is certain mechanical properties of a material that indicates the maximum resistance of material which is acceptable for the material until it was damaged or broken. The fracture determination test conducted in this study aims to determine the maximum resistance of the artificial tooth base to the load given until the fracture. Figure 5 shows the effect of the filler concentration on the firmness of the broken denture base. Obtained fracture value at 0% addition of 46.704 MPa; 10% of 48.859 MPa; 20% by 45.447 MPa; and 30% of 45.191 MPa.

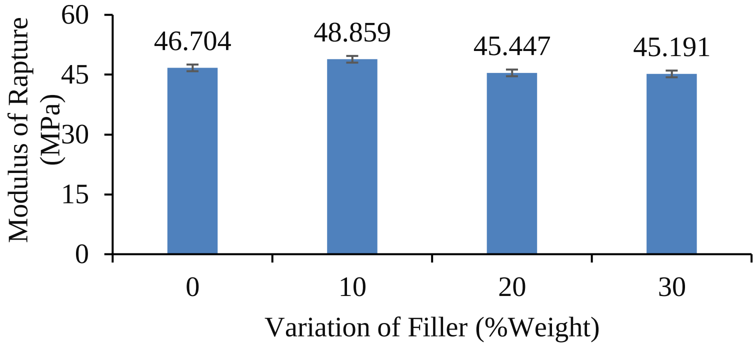
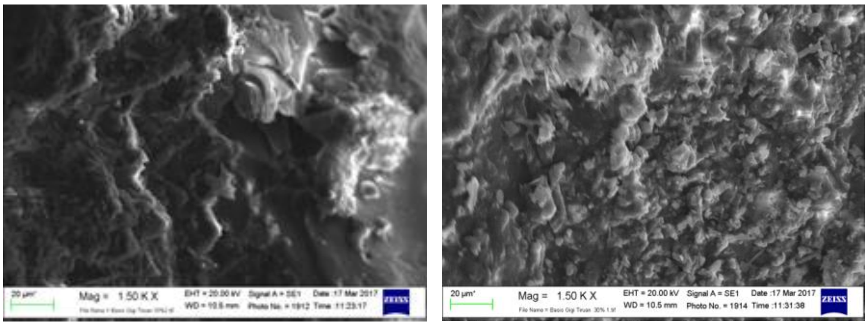



**Fig. 5 Effect of addition nanoparticle chicken eggshells filler to modulus of rupture (MOR) biocomposite denture base.**

From this study, the addition of above 10% filler concentration will cause the sample to become saturated thus decreasing the strength value of the sample. This is due to too much filler and causes the agglomeration of nanoparticles in the resin matrix [19]. The addition of 30% filler decreased the strength value due to the higher concentration of the filler may enlarge the interaction between the filling particles, resulting in the formation of agglomerates. The agglomeration that occurs due to the high filler concentration that causes the composite not to be homogeneously structured and at a certain stress point level to be detached from the matrix, resulting in a crack [20]. Small particle size as filler can increase flexural strength due to increased surface area of the particles, which results in high surface energy at the interface of the fill matrix [18].

### 3.6. Characterization of scanning electron microscope (SEM)

Characterization of Scanning Electron Microscope (SEM) was conducted to see the morphology of biocomposite denture base. Figure 6 shows the morphology fracture of the artificial tooth base of 10% eggshell nanoparticles has uneven and brittle surface fracture structures with fairly even distribution of particles. Figure 6(a) shows that there was no empty space or void and no agglomeration with the addition of 10% concentration of eggshell nanoparticles. Meanwhile, Fig. 6(b) shows the morphology of a 30% egg-shaped base of an eggshell nanoparticle having a rough and uneven cracked surface structure, many cavities or gaps are formed and so much concentration of particles in the matrix that causes agglomerate formation in the sample. The cavity or gap (void) formed on the composite can affect the bond between the filler and the matrix. The existence of voids can cause the matrix to not be able to fill in the blank space in the mold. If the composite receives a load, then the stress area will move to the void area so that will reduce the composite strength [21]. The agglomeration that occurs is caused by the excessive concentration of fillers used so that the accumulation of fillers within a matrix area, which can reduce the strength of the denture base.



**(a)** **(b)**

**Fig. 6. (a) Characterization of scanning electron microscope (SEM) biocomposite denture base: (a) 10% chicken eggshells with 1500x enlargement, (b) 30% chicken eggshells with 1500x enlargement.**

## 4. Conclusions

The addition of nanoparticle chicken eggshells filler in the acrylic resin for denture base obtains a biocompatible material. It could be proven from the increasing of mechanical properties of biocomposite denture base. Fourier Transform Infrared (FTIR) of denture base with nanoparticle chicken eggshell showed results the appearances of autenthic functional groups which indicated calsium presence in certain wavenumber.

Based on XRD showed crystalinity index of the nanoparticle eggshell obtained 87.8% with diameter of particle was 47 nm. Modulus of Elasticity (MOE) and Modulus of Rupture (MOR) of biocomposite was increasing with the addition of chicken eggshells with optimum value are 2.571 GPa and 48.859 MPa. The addition of 10% filler has better result when compared with the addition of 30% filler.

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