Multifunctional Bioceramics for Innovative Therapy

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Abstract. This study prepared Magnesium-Partially Stabilized Zirconia (Mg-PSZ) filler synthesis and direct foaming technique using egg whites, and impregnated by PMMA. The results were evaluated systematically by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM). XRD results denote that the powder sample of MgPSZ was successfully formed with various crystal size of tetragonal and monoclinic phase. SEM and TEM observations revealed that nanoparticles MgPSZ were in spherical and long rounded shapes. Furthermore, SEM observation revealed that the direct foaming method were also successful in the formation of porous structures which favourable for impregnation process by PMMA. The use of egg whites as a polymer precursor in both methods demonstrates that porous specimens contained nano-sized, predominantly tetragonal, Mg-PSZ powders were successfully synthesized. This shall yield an interesting prospect towards cheap, reliable, and biocompatible product to resemble the modulus elasticity of dentin.

Introduction

The thickness of the remaining dentin is a crucial factor to root fractures, commonly tooth will gradually weakened due to the loss of crown structure after endodontic treatment. Therefore, it should be noted that the ideal material used to restore should have a modulus of elasticity that resembles dentin [1, 2]. In order to manage that, zirconia post was developed because it offers higher strength and aesthetics compared to other materials, and also chemically stable [3]. However, the presence of excess load can also cause the root fracture failure [1, 2].

Small amount of other metal oxide that introduced to the zirconium oxide crystal structure will serve as a stabilizer that will make the tetragonal structure remains stable at room temperature, which is known as transformation toughening mechanism [4, 5]. Magnesium is one type of common stabilizer that is easily available and often used in biomedical applications despite its shortcoming in porosity and large particle size, about 30-60 µm [6, 7].

MgPSZ (Magnesia Partially Stabilized Zirconia) nanoparticle can be synthesized via sol-gel technique with a modified Pechini method using polymer precursors to produce a relatively low
cost ceramics in low heat temperature with homogenous composition and high purity results [8]. The common polymer precursors are metal oxides, ethylene glycol, and citric acid. Ethylene glycol will facilitate the polymerization of metal oxide with citric acid became metal citrate [8]. However, this unique property is also possessed by the egg white or albumen. Egg protein contains amino acid polypeptide chain that can provide the amine group and carboxyl to enable it in binding the polymer chains [9, 10, 11].

Excess strength as mechanical consequences of the nanomaterial MgPSZ can be reduced by performing direct foaming technique, utilizing egg white that will increase the material porosity. The acrylic resin is then impregnated through the pores to lower the modulus of elasticity of the material similar to dentin [2, 12].

Materials and Method

MgPSZ Filler Synthesis. The synthesis of MgPSZ filler is aimed to obtain a small, homogenous particles of ceramic powder. The common MgPSZ particle size ranges between 30-60 μm [7]. MgPSZ particles should be dominated by the tetragonal phase in order to achieve the transformation toughening mechanism. This is when the tetragonal phase of MgPSZ changes into the monoclinic phase while expanding volume and closing cracks. The macroscopic effect of this mechanism is the increase of fracture toughness of the material.

The egg white ability to provide amine group and carboxyl is utilized to obtain the similar characteristic to the ethylene glycol to bind the polymer chains. Generally, polymerization reaction with the formation of amorphous resin occurs at a temperature of about 150 °C and will burn at 250 °C [16]. This study adapted a modified Pechini Method to generate amorphous resin to improve the heating experiment at lower temperature (90 – 100 °C).

Zirconium (IV) chloride was firstly dissolved in aquabidest (distilled water). In order to precipitate the zirconium hydroxide, ammonium hydroxide (1M) is needed to be added into the solution, then centrifuged it with aquabidest in order to completely remove the ammonium chloride solution before then dissolved with nitric acid (1 M) to produce a clear solution of zirconium nitrate [11]. Same procedures were applied to magnesium chloride to provide a clear solution of magnesium nitrate.

The nitrate solutions were mixed then stirred for 5 minutes, considering stoichiometry of ZrO₂-8 mol% MgO₂. The solution was transferred to a 2000 ml beaker glass on the top of container filled with vegetable oil. When the heat reached 80°C, 0,05 M Citric Acid (CA) was added with CA: total oxides (TO) molar ratio (CA : TO) of 4 : 1. The total oxides denoted the sum of ZrO₂ plus MgO₂ in the final ceramic powder [11, 13].

While the solution was stirred, egg whites were mixed by ultra stirring on 10.000 rpm with molar ratio 10 : 1 of citric acid. After the temperature of the solution reached 90°C, the egg whites were then added to the solution, stirred until producing char flakes for 2 hours and left at constant temperature of 200°C for 1 hour to be hardened. The black mass then ground in mortar and pestle then calcined at temperature of 700 °C for 2 hours with direct cooling to obtain MgPSZ white ceramic powder [11, 13]. The powder was then homogenized using an ultrasonic homogenizer for about 5-10 minutes to obtain smaller and homogenous particles.

Direct Foaming Process. This method is carried out to create more pores in the MgPSZ filler that can reduce the strength and at the same time provide the needed space to inject the PMMA. The desired result is the MgPSZ filler with a similar size and well distributed pores. MgPSZ filler was mixed with egg white to obtained a slurry with compositional ratio of 2 : 1. This slurry mixture was moved into a 6 mm thick and 12 mm diameter size mold that was coated by lubricant and heated in the oven at 100 °C temperature for about 1 hour until dry and stiff. The specimen was then removed and reheated inside a furnace with 1300 °C temperature for 2 hours. As a result, 50% shrinkage of a porous specimen with 3 mm thick and 6 mm diameter size was obtained.
**PMMA Impregnation Process.** This technique is applied to fill the pores created by the direct foaming with PMMA in order to achieve similar modulus elasticity to dentin. PMMA (Polymethyl Metacrylate) solution was prepared from liquid MMA monomer and polymer powder containing 2 wt% of benzoyl peroxide as a polymerization initiator. Specimen was then immersed in PMMA liquid inside a mixing jar and placed inside the oven with a temperature of 60°C for 1 week [14] to optimize the polymerization during the impregnation process.

**Characterization.** The existing phase of the synthesized filler powder was analyzed by a Phillips X-rays Diffractometer. Surface microstructure of the specimen were analysed using Scanning Electron Microscope-SEM (JEOL) while the MgPSZ powder morphology and size were observed using Transmission Electron Microscope-TEM (JEM 1400). SEM was also used to analyze the results from direct foaming technique with the egg white surfactant prior to be impregnated by Polymethyl Methacrylate (PMMA).

**Results and Discussion**

Nanoparticles Magnesium Partially Stabilized Zirconia (MgPSZ) 8% that has been analyzed using an X-Ray study shows a diffractogram on Figure 1. The majority crystal phase is tetragonal with the size of 8-26 nm, while the rest of the monoclinic crystals range from 18-42 nm. The result confirms that the structures of the protein component of egg white in the form of amine and carboxyl groups are able to form a polypeptide bond through polymerization to produce ceramic nanoparticles at a low temperature [8, 11, 15]. These results is similar to the use of ethylene glycol by the Pechini method which is able to produce an agglomeration powder with crystal size 10 nm on yttria stabilized zirconia [8, 16].

![Fig. 1. X-ray Diffraction Analysis Result of MgPSZ Powder.](image)

The typical SEM image of the MgPSZ sample heated at 700 °C is shown in Figure 2. The particle structures are homogenous with spherical shape and equal sized. However, they are still showing agglomeration.

The BFI (Bright Field Image) and DFI (Dark Field Image) images in Figure 3a and 3b show that the synthesized particles have spherical and long round shape; size ranges from 10-70 nm. The EDP picture in Figure 3c corroborates the XRD results which indicate that the majority of the crystal structure is tetragonal which will certainly help improve the mechanical properties due to the transformation toughening mechanism to prevent the propagation of cracks [7, 17].
In the process of synthesis using a modified Pechini method with inorganic precursors zirconium and magnesium nitrate (ZrO(NO$_3$)$_2$ and Mg(NO$_3$)$_2$), egg whites acts as polymer precursors and citric acid is used as a chelating agent for binding various cation by forming polybasic acid. Polymerization reaction with egg whites forms anhydride bond and water as a byproduct. When the mixture is heated, polyanhydrides occur and produce a homogenous solution with metal ions distributed through the organic polymer matrix, i.e. egg whites. The solution will form resin by evaporation of excess water.

Generally, polymerization reaction with the formation of amorphous resin occurs at a temperature of about 150 °C and will burn at 250 °C [16]. However, this experiment result via modified Pechini Method is able to form amorphous resin at 90 – 100 °C and charred at 200 °C assisted with an oil bath in the form of vegetable oil [13], so it improves the heating experiment using lower temperatures.

Fig. 2. The SEM Result of MgPSZ Powder.

Fig. 3. TEM Result of MgPSZ Sample (a) Bright Field Image, (b) Dark Field Image, (c) Electron Diffraction Pattern Image.

Fig. 4. SEM Results of the Specimen (a) before, and (b) after Impregnation.
Porosity is an important aspect to be considered in making an excellent dental post. In many cases, the strength possessed by zirconium post can lead to root fracture [1, 2]. Samples of MgPSZ powder which has been successfully synthesized in this study has been successfully developed into a porous specimen by direct foaming techniques. Components of the egg white proteins, ovomusin and ovoglobulin, serve as the bubbling agent of egg white [12, 15] to generate porous surface, that later can be impregnated [15]. SEM images (Figure 4a) from the MgPSZ powder samples with egg whites demonstrate the porosity created from the direct foaming technique. However, the pore size varies and they are still not perfectly distributed.

Before the impregnation process, the specimens from direct foaming process were heated at 1300 °C inside closed furnace to optimize the sintering which occurred at 1250 °C [18]. Impregnation process is performed using the MMA solution of heat-cured acrylic resin with PMMA powder that contain 2 wt% of benzoyl peroxide initiator, and then stored in a preheated oven at 60°C for 1 week [14]. The purposes of preheated process are: (1) in order to provide enough time for the benzoyl peroxide molecules to decomposes and generate free radicals [17]. Each of these free radicals reacts with monomer molecules to initiate polymerization. (2) It will also give sufficient time to the resin to fill the pores via capillarity phenomena.

Figure 4b shows the result of the impregnation process. An interface layer has been created between the MgPSZ specimen and PMMA resin. This suggests that the pores are not fully impregnated. There are two potential causes to it: (1) the pore size is still relatively small compare to the PMMA molecules. Potentially, smaller and less viscous PMMA molecules will improve the process. (2) Variation in pore size and their distribution may reduce the permeability of the specimen. It is highly possible that the optimum composition of the egg white protein has not been fully attained during the experiment.

Therefore, several points need to be address in the future to improve the impregnation process. The PMMA molecules are unable to precipitate inside the pore using a traditional impregnation process. To achieve a better and efficient impregnation, it is required to know the effective porosity of the sample in order to predict the theoretical maximum solution that can be impregnated [19]. The selection of similar impregnation materials but has a lower molecular weight serves as an alternative to the impregnation process in order to maximize the capillarity phenomena.

Conclusions

The use of egg whites as a polymer precursor in a sol-gel technique demonstrates nano-sized Mg-PSZ powders with the majority of tetragonal crystals were successfully synthesized. Direct foaming technique utilizing egg whites has also greatly improved the specimen porosity. Although more work should focus to improve the impregnation process, the result of this study shall yield an interesting prospect towards cheap, reliable, and biocompatible product to resemble the modulus elasticity of dentin.

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References


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**Hardness evaluation of dental composite with ceramic fillers**
Djuhstana, N., Haqatinningsah, Z., Karina, E., (..), Hardiansyah, A., Sunandar, B.
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