Synthesis of Ca-Psz nanoparticles using sol-gel technique with chitosan as a dispersant for raw materials restoration and dental rehabilitation equipment

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ABSTRACT

Introduction: Zirconia (ZrO_2) is a metal-free substance that rapidly improving as dental materials that has a good properties which are high biocompatibility, esthetics, and strength. Addition of a stabilizer like CaO will increase the mechanical properties of zirconia due to the transformation toughening. **Methods:** The Calcia Partially Stabilized Zirconia (Ca-PSZ) nanoparticles can be synthesized by using sol gel technique. This method makes easier to control the purity, homogeneity and physical characteristics at low temperature. This method consists of two stages, hydrolysis and condensation. The precursor were used Zirconium Chloride ($ZrCl_4$) with 0,1 M concentration and Calcia as stabilizer with 7% concentration. The addition of Calcia will help the tetragonal crystals forming at low temperature. Calcination temperature was used 900^o C. To prevent conglomeration or agglomeration, dispersants are needed. One of the dispersants available is chitosan. **Results:** X-Ray Diffraction (XRD) analysis identifies that there are tetragonal and monoclinic phase with a percentage of 85% and 15% perspectively for sample without using chitosan and 100% tetragonal for sample that using chitosan. Analysis of Scanning Electron Microscope (SEM) results that particles with chitosan are more homogenous and dispersed with smaller size produced compared to particles without chitosan. **Conclusion:** From the results of the analysis, Ca-PSZ with sol-gel technique can produce nanoparticle and addition of chitosan can dispersed nanoparticles that could be used as material restoration and rehabilitation component in dentistry.

Keywords : Ca-PSZ, Nanoparticles, Chitosan, Dispersant, Sol Gel

INTRODUCTION

Ceramic material specially developed for medical and dental purposes is called bioceramics. One example of bioceramics is zirconia. Over the past decades, zirconia technology has developed rapidly as a metal-free dental material that has high biocompatibility, aesthetic value, and strength.[1,2,3] Excellent molecular stability can be achieved by combining zirconia crystals with alkali metal oxides such as MgO, CaO, or Y2O3 as a stabilizer. The addition of this stabilizer has a role during the process of transformation toughening works to prevent cracking so that the zirconia crystals becomes stronger. The addition of zirconia with alkali metal oxides is called Partially

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Stabilized Zirconia (PSZ).[2,3,4,5] The use of PSZ very much begins from the fields of industry, medicine, and dentistry. Since 1990, this form of PSZ has been introduced as a dental material because of its excellent strength and good fracture resistance. PSZ gained popularity in many industries because of its high resistance, fracture strength (7-8MP), flexure strength (0.9-1.5GPa), corrosion resistance and good thermal conductivity.[3,5]

In dentistry, the use of PSZ is as a composite filler, crown and bridge, orthodontic bracket, and implant. Research on PSZ in Dentistry is often carried out in the prosthodontics field as a crown and bridge to replace porcelain fused metal (PFD) and framework.[2,5,6]

Metal oxide stabilizers such as MgO and Y2O3 have deficiencies, including MgO not very well used in dentistry as it produces large porosity and granular shape (30–60μm) which influences auxin resistance1. (Denry and Kelly, 2007) While Y2O3 is a rare and expensive material. Both metal oxides also have more toxic properties than CaO. CaO, a metal oxide that has the advantage over other stabilizers because it is similar to bone-forming material7 (Shtansky, 2003) and thus is more biocompatible. CaO is also cheaper and easier to obtain. This CaO stabilizer can also prevent cracking on its crystal structure.[3,4]

There are various ways of making PSZ; in this study, the sol-gel technique was chosen. This technique is commonly used in metal oxides and its advantages can facilitate the control of purity, homogeneity, and physical characteristics at low temperatures. This technique can also be used to design microstructures so that particle size can be adjusted.[8,9,10] In the manufacture of PSZ particles can be agglomerated. Prevention needed are dispersants, one of which is chitosan. Chitosan is an ingredient derived from natural ingredients such as shrimp shells containing chitin. Chitosan is used so that particles can be well dispersed or agglomeration does not occur because chitosan makes a particle does not stick to other particles.[10,11,12]

Based on the explanation above, the author is interested in researching the manufacture of Partially Stabilized Zirconia based on restorative materials to obtain nanometer particle sizes from Ca-PSZ by using sol-gel and chitosan techniques as dispersing agents. The results of this synthesis will be characterized by using X-ray Diffraction (XRD) to see the zirconia crystal phase and Scanning Electron Microscope (SEM) to see the morphology and microstructure including the size of zirconia particles synthesized.

METHODS

The type of research is a quasi-experimental study with qualitative and quantitative analysis with the Partially Stabilized Zirconia (PSZ) nanoparticles and observation of the sample characteristics using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The samples used in this study were two nanoparticle specimens consisting of powder-formed Ca-PSZ with the addition of 1% chitosan, powder-formed Ca-PSZ without the addition of 1% chitosan.

Figure 1. Tools used in the making of Ca-PSZ nanoparticles, (1) 250 ml chemical beakers, (2) 250 ml measuring cups, (3) spatulas, (4) pipettes, (5) mortars and pestles, (6) digital scales (Mini Pocket Scale MA 100A sensitivity 0.01 g), (7) Magnetic stirrer, (8) Ultra turra stirrer (IKA

T25 Digital Ultaraturrax max. 24000 rpm), (9) Furnaces, (10) Ultrasonic Homogenizer (UP50H Hielscher max 12000 Hz). Figure 2 Materials used in the preparation of Ca-PSZ nanoparticles, (1) Zirconium Chloride (ZrCl4) as precursors, (2) Aquabides as solvents, (3) Ca (NO3) 2 as stabilizers, (4) Acetic acid as solvents, (5) Aqua Demineralized (Aqua DM) as a solvent, (6) Ethanol as a solvent, (7) Chitosan as a dispersant.

RESULTS

The data obtained is the result of the characterization using XRD and SEM. The data from this study were used to analyse the characteristics such as the crystal structure formed, size of the crystals, morphology and particle size of samples that have been synthesized by sol-gel technique.
XRD characterization is useful to identify the phase or character of the sample made. From this result, we can determine whether the desired tetragonal phase is formed or not. The calcination temperature used in this study was 900°C. The crystalline phase formed was determined by comparing the diffraction angle of the peak XRD results with the database of the X-Powder

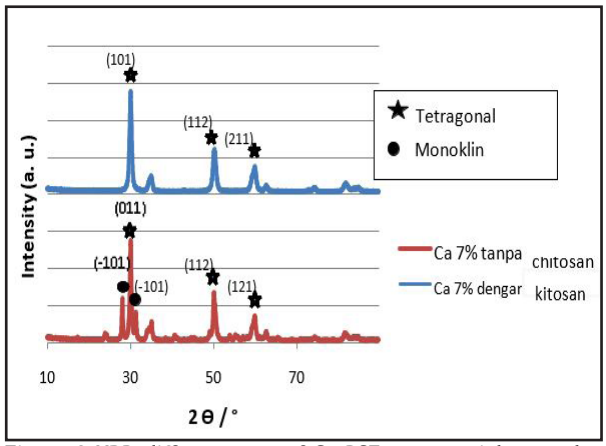

Figure 3 XRD diffractogram of Ca-PSZ nanoparticle samples using chitosan and without using chitosan

software. The X-powder used is Ver.2004.04.70. PRO with tetragonal crystal reference number = 42-1464 and monoclinic = 37-1484. Tetragonal phase nor monocline appears in the sample, as shown in figure 3. From Figure 3, it can be seen that there are differences in crystals formed in the sample using chitosan and without chitosan. In samples with chitosan, the tetragonal crystal structure at the peak of the highest diffraction angle (2θ) was 30,095°, 50,280°, and 60,025°. Samples without chitosan showed tetragonal crystals formed at a diffraction angle of 30.225°, 50.140°, 59.970°. The microstructure of the sample particles can be seen and observed using a Scanning Electron Microscope (SEM) tool. This tool is used to find the morphology and growth of particles that occur. With the calcination temperature used at 900°C, an SEM image found in CaPSZ samples with the addition of chitosan and without chitosan, it can be seen in Figure 4. Ca-PSZ particles with chitosan are more homogeneous and dispersed compared to without the addition of chitosan.

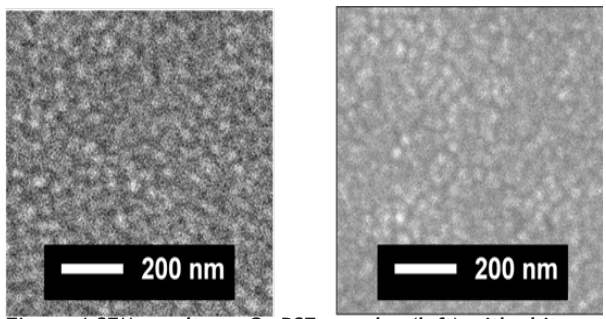

Figure 4 SEM results on Ca-PSZ samples (left) with chitosan and (right) without chitosan

DISCUSSION

Synthesis of nanoparticles carried out in this study referred to previous studies (Hermawan, 2010). During the last research, nanoparticle synthesis using Y2O3 stabilizer with sol-gel technique.

The research was successful in synthesizing Y-PSZ nanoparticles, while in this study it was incorporated using the same method but with a different stabilizer, CaO. In the process of making selected nanoparticles using the sol-gel method that includes stages that consist of hydrolysis and condensation.

The hydrolysis stage occurs when the precursor (ZrCl4) reacts with aqua bides with the following reaction. ZrCl4 + 4H2O Zr(OH)4 + 4HCl At this stage of hydrolysis, there is a break of ZrCl4 metal bonds by water to form metal hydroxide compounds, called Zr (OH)4. The result of the hydrolysis reaction is HCl, which is a weak acid with a pH = 2. Colloid sol Zr (OH)4 occurs when the pH must be at 2 to 3 as shown. The area that is not shaded is when the solution occurs. The

line between the two regions shows when colloids occur. For Zr (OH)4, if the pH is less than 2 (white area), then a solution is formed; If the solution is formed, the condensation reaction occurs very slowly. However, if the pH is more than 3, the condensation reaction will occur more quickly, and larger particles are formed.[10]

The addition of CaO affects the mechanical properties of zircons. Without the addition of CaO or stabilizer zirconia will have a low mechanical property and can quickly turn into a monocline crystal phase at room temperature. This addition of CaO helps zirconia to have a tetragonal crystal phase at room temperature and has high strength. Chitosan acts as a surfactant that acts as a zirconia particle wrapper in the stage before calcination is carried out. Chitosan dissolved in acetic acid makes chitosan to have an amino group (NH2) and will be cationic (affirmative).

ZrCl4 hydrolysis reaction results in the form of Zr(OH)4 which are anion (negative), due to the OH-group. When chitosan is added, the surface of the negatively charged particles will be immediately covered by positively charged chitosan. The surface of the particles that are covered with chitosan will cause the growth of the particles to stop. The result is particles that have become smaller in size. The effect of the addition of chitosan will also cover the surface of the particles and prevent contact with other particles, thereby preventing agglomeration.
The particles formed will be more homogeneous and well dispersed. Therefore chitosan in this research is called dispersant.

Figure 3 shows the differences in the structure of the crystalline phase formed in the Ca-PSZ sample. In samples with the addition of chitosan, visible aspects formed purely tetragonal. In the x-powder software, the percentage of the tetragonal crystalline phase is 100%. Thus, it proves that the sample has a single tetragonal crystal. Samples without chitosan observed as the tetragonal crystal and monocline crystal. This monocline crystal appears with the name baddeleyite.

The percentage of x-powder showed a tetragonal phase of 85% and a monoclinic crystal phase of 15%. So samples without chitosan have a multi-phase, namely monoclinic and tetragonal phases. The effect of chitosan will make the Ca-PSZ particles dispersed, thus helping the CaO stabilizer work optimally; therefore; as a result, it forms a tetragonal crystal. Samples without chitosan allow agglomeration to inhibit the formation of crystals; thus, CaO stabilizers do not work optimally; as a result, it forms tetragonal and monocline crystals.

Previous studies have shown there is an effect of calcination temperature in the formation of the crystalline phase. The results of the survey stated that Ca-PSZ calcined at temperatures of 600°C, 800°C and 1000°C only formed the cubic phase and at temperatures of 1300°C, 1400°C, and 1500°C formed tetragonal and monoclinic phases.[13] From Figure 2.7 about the ZrO2-CaO equilibrium phase, it is also seen that the addition of temperature and composition affects the crystalline phase formed.

The size of the crystals in the chitosan sample is smaller than 15 nm, while the example without chitosan is 20 nm. The size of the glasses with chitosan is shorter because the nature of chitosan when encapsulating particles makes the voltage between particles decrease.

Figure 4 shows the differences in the results of characterization with SEM in the Ca-PSZ nanoparticle samples with the addition of chitosan and without the addition of chitosan. Particle size can be calculated from SEM images with 100,000x magnification. However, calculations using SEM images are not very accurate because the image quality is not very clear.

Particle size calculation can be done with SEM results. The scale comparison at 100,000x magnification used to determine that the particle size is 0.1 μm. Particle size calculation is done by drawing a diagonal line in the SEM image and obtained a diagonal line length of 160mm, then counted the number of particles along the line obtained as many as 44 particles.

After the results are received, the length of the diagonal line is divided by the number of particles obtained. Then the average particle size in the image is 3.64mm. Furthermore, the average quantity of the particles is adjusted to a scale of 0.1μm, while 0.1μm = 100nm = 10mm. Then the average particle size in the sample is 36.4 nm. In samples, without chitosan, the particle size is calculated in the same way through SEM images. A 100,000x magnification scale comparison is used

to find out the particle size of 0.1 µm. Particle size calculation is done by drawing a diagonal line on the SEM image; the length of the diagonal line is 160mm. The number of particles along the path is calculated as many as 38 particles.

After the results are obtained, the length of the diagonal line is divided by the number of particles obtained. Then the average particle size in the image is 4.21mm. Furthermore, the average quantity of the particles is adjusted to a scale of 0.1µm, while 0.1µm = 100nm = 10mm.

Then the average particle size in the sample is 42.1nm. From the results of the above calculation, the particle size of Ca-PSZ with chitosan is smaller than Ca-PSZ without chitosan. Ca-PSZ particles with chitosan appear more homogeneous and dispersible compared to without the addition of chitosan.

CONCLUSION

Based on the results from the research conducted, it can be finalized that Ca-PSZ nanoparticles can be synthesized by sol-gel technique and the addition of chitosan influences the dispersion of nanoparticles formed with a single tetragonal structure.

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