THE EFFECT OF CHITOSAN SOLUTION ADDITION ON THE SIZE OF NANO CERAMIC PARTICLES IN ZrO_2-Al_2O_3-SiO_2 SYSTEM THROUGH BOTTOM-UP METHOD AS DENTISTRY RAW MATERIAL

(PENGARUH PENAMBAHAN LARUTAN KITOSAN TERHADAP UKURAN PARTIKEL KERAMIK NANO SISTEM ZrO_2-Al_2O_3-SiO_2 MELALUI METODE BOTTOM-UP SEBAGAI MATERIAL BAKU KEDOKTERAN GIGI)

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ABSTRACT

Ceramics is a dental material used often because of its relatively good strength and aesthetic properties. Ceramics such as zirconia, alumina, and silica have different characteristics and have been synthesized using a bottom-up method separately. Recently, many studies have used chitosan solution to help synthesize nanometer-sized ceramic materials processed using the bottom-up method. This study aims to produce ZrO_2-$A1_2O_3$-SiO_2 nanoparticle ceramics, which were synthesized simultaneously using the bottom-up method, and to see the effect of

volume concentration of chitosan solution on the resulting ZrO_2-$A1_2O_3$-SiO_2 ceramic particles. The composition ratio of ZrO_2:Al_2O_3:SiO_2 used is 3:1:1 with a concentration of 0.05M and a total volume of 500ml. The chitosan solution was added with a volume percentage of 0%, 5%, 10%, 15%, and 20%, respectively, and was named samples A, B, C, D, and E. The XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscopy) characterization of the five samples showed nano-sized particles, which were 87 nm, 85 nm, 81 nm, 76 ran, and 76 nm. SEM characterization results show that sample A's particle distribution is not very visible; the particle distribution is only seen in samples B, C, D, and E, while the best particle distribution is seen in sample C. This study concludes that the optimal volume concentration of adding chitosan solution to produce nano-sized ZrO_2-$A1_2O_3$-SiO_2 ceramics with good particle distribution is 10% by volume percentage.

Keywords: ceramic system; chitosan; nanoparticles; particle distribution; ZrO_2-$A1_2O_3$-SiO_2

ABSTRAK

Keramik merupakan salah satu material kedokteran gigi yang cukup sering digunakan karena sifat kekuatan serta estetikanya yang relatif baik. Keramik seperti zirkonia, alumina dan silika memiliki karakteristik yang berbeda-beda dan pernah disintesis menggunakan metode bottom-up secara terpisah. Belakangan ini banyak penelitian yang menggunakan larutan kitosan dalam membantu mensintesis material keramik berukuran nanometer yang diproses menggunakan metode bottom-up. Penelitian ini bertujuan untuk menghasilkan keramik partikel nano sistem ZrO_2-$A1_2O_3$-SiO_2 yang disintesis secara bersamaan menggunakan metode bottom-up serta melihat pengaruh konsentrasi volume larutan kitosan pada partikel keramik ZrO_2-$A1_2O_3$-SiO_2 yang dihasilkan. Perbandingan komposisi ZrO_2:$A1_2O_3$:SiO_2 yang digunakan adalah 3:1:1 dengan konsentrasi 0,05M dan volume total 500ml. Larutan kitosan ditambahkan dengan persentase volume

masing-masing 0%, 5%, 10%, 15%, 20% dan diberi nama dengan sampel A, B, C, D dan E. Hasil karakterisasi XRD (X-Ray Diffraction) dan SEM (Scanning Electron Microscopy) kelima sampel tersebut memperlihatkan partikel berukuran nano yang secara berurutan yaitu 87 nm, 85 nm, 81 nm, 76 ran dan 76 nm. Hasil karakterisasi SEM memperlihatkan gambaran distribusi partikel sampel A tidak begitu terlihat, distribusi partikel hanya terlihat pada sampel B, C, D dan E sedangkan distribusi partikel paling baik terlihat pada sampel C. Kesimpulan penelitian ini adalah konsentrasi volume optimal dari penambahan larutan kitosan untuk menghasilkan keramik ZrO_2-$A1_2O_3$-SiO_2 berukuran nano dengan distribusi partikel yang baik adalah pada persentase volume 10%.

Kata kunci: *distribusi partikel; keramik sistem ZrO_2-$A1_2O_3$-SiO_2; kitosan; partikel nano*

INTRODUCTION

Ceramic materials, widely used in prosthodontics and conservation and the long term, have shown the advantages of metal- and metal-ceramic-based restorations.[1] Today, various ceramic materials have been developed and used to manufacture dental restorations using modern technology. The increase in material stability in several ceramic compounds triggers the use of ceramic material applications as raw materials for making crown bridges, inlays, onlays, and veneers.[2] Some examples of ceramics that are widely used as raw materials in dentistry include silica (SiO_2), alumina (AI_2O_3), and zirconia (ZrO_2).[3-5]

Zirconia is a material with high flexural strength, low thermal conductivity, hard, heat resistant, opaque, and biocompatible with body tissues. The flexural strength of zirconia can be increased by adding stabilizers such as yttria (Y_2O_3), calcia (CaO), magnesia (MgO), lanthane (La_2O_3), cheerful (CeO), and alumina (AI_2O_3).[6] Alumina is used as a stabilizer; it can also be used as a reinforcement for zirconia (alumina-toughened zirconia). Opaque alumina will produce less aesthetic restorations when combined with zirconia only. For this reason, other materials with translucent properties, such as silica, are needed to improve the resulting material's aesthetic

properties.[7.8]

Research has been carried out using zirconia, alumina, and silica as raw materials for manufacturing dental restorations. In this study, zirconia, alumina, and silica were synthesized using the sol-gel technique, then mechanically combined as raw materials to manufacture dental restorations.[9.10] However, zirconia, alumina, and silica materials are known to be synthesized in a system form, namely as refractories in glass furnaces and gas sensors.[11] One method that has been used to synthesize zirconia, alumina, and silica ceramics is the bottom-up method. The sol-gel technique is a technique that uses the liquid bottom-up method, which is widely chosen in synthesizing ceramics because it is more efficient and inexpensive with simpler tools than other synthesis techniques.[12.13] Synthesis of ceramic materials through the sol-gel technique is sometimes added with a chitosan solution as a dispersant to prevent agglomeration of particles so that the resulting ceramic particles will be uniformly/homogeneous in nano size.[14.15] This research aims to produce ceramic nanoparticles ZrO_2-$A1_2O_3$-SiO_2 system, which was synthesized simultaneously through the bottom-up method (sol-gel technique), and to see the effect of concentration.

METHOD

This research design was descriptive qualitative. The materials used in this research include zirconium chloride ($ZrCl_4$), aluminum nitrate ($Al(NO_3)_3$), and TEOS obtained from Sigma Aldrich. The research procedure begins with the manufacture of a chitosan solution followed by the synthesis of nano-ceramic systems. The ZrO_2-$A1_2O_3$-SiO_2, then XRD characterization of the sample to determine resulting ceramic crystals and SEM to view the distribution of ceramic particles. The chitosan solution was prepared in the following way: mix 6 ml of acetic acid with 294 ml of aquabides so that acetic acid with a concentration of 2% 100 ml was produced. Enter the chitosan powder into the solution, and stirrer for 30 minutes until it dissolves to obtain a chitosan solution. Synthesis of the ZrO_2-$A1_2O_3$-SiO_2 nano ceramic system was obtained in the following manner: Mix the three precursors zirconium chloride ($ZrCl_4$), aluminum nitrate ($Al(NO_3)_3$) and TEOS with aquabides for 45 minutes and treated without and with the addition of chitosan solution. The sample without adding chitosan solution as control was called sample A. The next sample was added 5% vol of chitosan solution of the total volume for sample B, 10% vol for sample C, 15% vol for sample D, and 20% vol for sample

E. Sample was then dried in an oven at a temperature of 110 °C until dry, and a crust is formed. The sample was calcined in the furnace at a temperature of 900 °C for 2 hours. After calcination, the ceramic result was ground with a mortar and ethanol solution until smooth and then homogenized using an ultrasonic homogenizer for 6 x 5 minutes. The sample was dried again in an oven at 110 °C.

RESULT

Figure 1 shows an XRD image of a ceramic sample of the resulting ZrO_2-$A1_2O_3$-SiO_2 system. XRD analysis is assisted by using Xpowder software to read XRD graphs. Sample A - E XRD graph shows two identified crystallite phases: tetragonal zirconia and - alumina. Tetragonal crystallite peaks were identified at diffraction angles of 30.2°, 35.3°, 50.5°, 56.6°, and 60.2° (JCPDS 42-116). The crystallite peaks of – alumina were identified at the diffraction angles of 35,102° and 43.341° (JCPDS 46-1212). The XRD graph of the AE sample shows the difference in the percentage of tetragonal crystallites produced and the average crystallite size. The samples of AE contained tetragonal zirconia crystallites were 86.2%, 87.5%, 85.7%, 84.6%, 85.5% of the total fraction and the crystallite sizes were 15 nm, respectively.

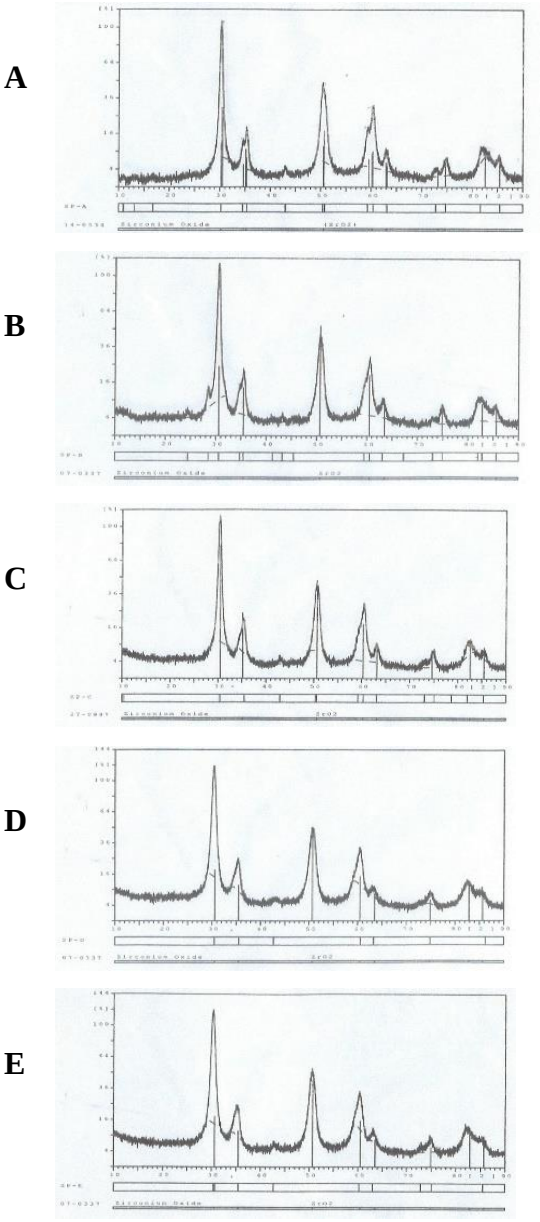

Figure 1. XRD characterization results.

The description of SEM characteristics is shown in Figure 2. The results of SEM characterization show the distribution of ceramic particles and particle size. The ceramic particles of sample C showed the best particle distribution among the other samples. In

some samples visible agglomeration of particles and impurities.

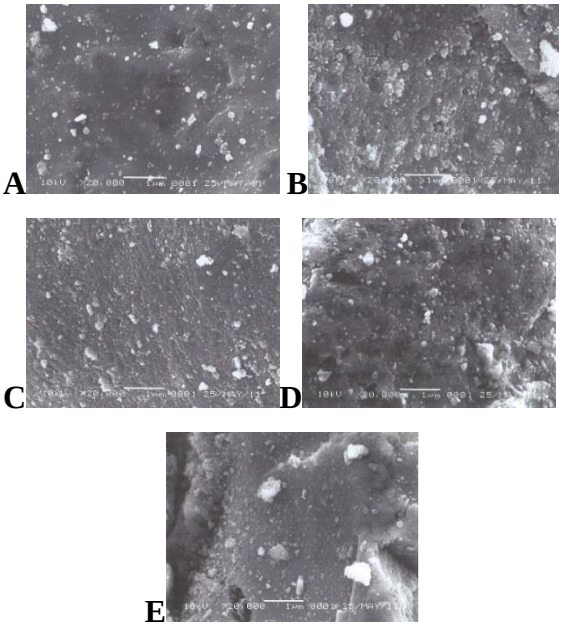

Figure 2. Results of SEM characterization.

DISCUSSION

In synthesizing ceramic nanoparticles with the ZrO_2-$A1_2O_3$-SiO_2 system, a bottom-up method with the sol-gel technique was used. The sol-gel technique consists of two reaction steps: hydrolysis and condensation.[16.17] In the hydrolysis stage, a reaction occurs between the precursors $ZrCl_4$, $A1(NO_3)_3$, and TEOS with aquabides, as follows:

The hydrolysis reaction of zirconia precursor (zirconium chloride) $ZrCl_4$:

$ZrCl_4 + 4H_2O \rightarrow Zr(OH)_4 + 4HC$.....(a)

Hydrolysis reaction on alumina precursor (aluminum nitrate) $Al(NO_3)_3$:

$Al(NO_3)_3 + H_2O \rightarrow Al(OH)_3 + H^{++} NO_3^-$ .....(b)

Hydrolysis reaction on silica precursor (Tetraethyl Orthosilicate) TEOS :

$Si(OC_2H_5)_4 + 4H_2O \rightarrow St(OH)_4 + 4C_2H_5OH$ .....(c)

In this hydrolysis step (formulas a, b, and c), the metallic bonds of $ZrC1_4$, $A1(NO_3)_3$, and $Si(OC_2H_5)_4$ are broken by water to form metal hydroxide compounds, namely $Zr(OH)_4$, $A1(NO_3)_3$ and $Si(OH)_4$. The condensation or polymerization stage is when the metal hydroxide powder that has been formed in the solution process binds to each other to form metal oxide compounds.[16] At this stage the authors suspect that alumina compounds that function as stabilizers can be substituted for zirconia lattices. In the condensation stage, inorganic chain growth occurs in the solution. Chitosan functions as a dispersant when dissolved. It can wrap ceramic zirconia, alumina, and silica particles so that the particles do not agglomerate before calcination. Chitosan dissolved in acetic acid makes chitosan have a cationic amino group (positive) -15 When chitosan is

added. The surface of the negatively charged particles will immediately bond and be covered by positively charged chitosan. The surface of the particles that have been covered with chitosan will cause the particle growth to stop and prevent agglomeration from occurring. As a result, the particles formed will be smaller.

The calcination process improves the morphology and degree of crystallinity of ceramics.[17] The XRD characterization results (Figure 1) show that the crystallites formed in all samples were tetragonal zirconia and -alumina crystallites. The peaks of the two crystallites in the five samples have diffraction angles and crystal orientations that are almost identical and depicted on similar characterization graphs. Tetragonal crystallites formed at 1170°C while -alumina crystallites are formed in the temperature range of 1050°C-1550°C. Still, both can form at a temperature of 900°C due to the nano-sized particle size due to the bottom-up method used.

The zirconia tetragonal crystallites produced in the five samples had a fraction of ± 85%. The zirconia monoclinic crystallites were stable at room temperature. It was not visible in the five samples using the xpowder software. The metastable tetragonal crystallites were maintained at room temperature. It was due to alumina ions being substituted in the zirconia lattice in the condensation process. The alumina ions carry oxygen vacancies in the zirconia lattice, so the crowded oxygen ions that cause the tetragonal to monoclinic phase change can be suppressed. It causes alumina to retain the tetragonal crystallites (of zirconia) which indirectly increases the flexural strength of zirconia.

SEM characterization results show that the AE samples' particle sizes are 87 nm, 85 nm, 81 nm, 76 nm, and 76 nm (figure 2). In the results of this characterization, the authors conclude that the higher the concentration of chitosan added to the process of making nanoparticle ceramics with the ZrO_2-$A1_2O_3$-SiO_2 system, the smaller the crystallite size produced.

The description of the particle distribution can also be seen in the SEM characterization. Sample A (figure 2) appears to be densified due to silica particles undergoing sintering to bind to zirconia and alumina particles. Due to the absence of chitosan content as a hydrophobic agent that can prevent contact between particles, the distribution of particles in this sample is not clearly visible. The results of SEM characterization in sample B show a fairly good particle distribution, but the distribution of particles formed is less even and homogeneous. Due to particle agglomeration. Researchers

suspect this is caused by a fairly low concentration of chitosan so that the particles not bound by chitosan experience agglomeration. The characterization of sample C shows that the ceramic particles are very well distributed/dispersed, where no agglomeration is seen in the image. The particles in this sample are evenly distributed and best distributed compared to other samples. The characterization of samples D and E showed that the ceramic particles were not evenly distributed/dispersed because there was a lot of agglomeration in the image. It was because the concentration of chitosan that is too high causes the ceramic particles formed to be too small so that the particles easily agglomerate. The particles in this sample are evenly distributed and best distributed compared to other samples. The characterization of samples D and E showed that the ceramic particles were not evenly distributed/dispersed because there was a lot of agglomeration in the image. The chitosan concentration is too high, causing the ceramic particles formed to be too small so that the particles could easily agglomerate. The particles in this sample are evenly distributed and best distributed compared to other samples. The characterization of samples D and E showed that the ceramic particles were not evenly distributed/dispersed because there was a lot of agglomeration in the image. The concentration of chitosan is too high causing the ceramic particles formed to be too small so that the particles easily agglomerate.

CONCLUSION

The optimal concentration to produce ceramic nanoparticles ZrO_2-$A1_2O_3$-SiO_2 system with the best description of particle distribution and can be used as raw material for dentistry is 10% chitosan concentration by volume.

CONFLICT OF INTEREST

The authors reported no potential conflict of interest.

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