The compositional observation of synthesized ZrO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} as dental composite fillers

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Abstract. One aspect of improvements in the field of restorative dental material properties is focusing on reinforcement of ceramic fillers. Indonesian researchers are encouraged to synthesize and fabricate dental materials product to promote national dental materials independency. This research aims to synthesize ZrO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} ceramic fillers and observed the composition of the particles using Scanning Electron Microscope (SEM) and Spectrum-Line Energy Dispersive Spectroscopy (EDS). The results show that the average particle size ranges between 0.5 – 150 μm. Zirconia formed as homogenous particles and the highest percentage among other elements. This composition shall provide the transformation toughening mechanism of ceramic dental composite as restorative materials.

1. Introduction

Physical and mechanical properties of restorative dental materials can be improved by filler reinforcement. These factors affect the clinical performance that will change the compressive and tensile strength, modulus of elasticity, and toughness. Dental composite is one of restorative dental materials used filler to reinforce the matrix using ceramic particles, such as glass, silica, and other metal oxides [1].

Ceramic fillers such as zirconia can be used on a variety of restoration needs such as crowns, veneers, bridge frameworks as well as reinforced materials. Zirconia (ZrO\textsubscript{2}) is a widely used ceramic material in various fields from electronic equipment to the field of dentistry. Zirconia is a crystalline dioxide from zirconium [2, 3]. Its mechanical properties are similar to metals and their colour is similar to tooth. Zirconia crystals consist of three types depending on temperature i.e. monoclinic (M), cubic (C), and tetragonal (T). Pure zirconia crystals at room temperature are in monoclinic form, however, from 1170°C to 2370°C the crystalline structure becomes tetragonal before transforming to cubic at above 2370°C until its melting point [2-4].

At room temperature, tetragonal and cubic crystalline structures are unstable and tend to transform into monoclinic. ZrO\textsubscript{2} mixtures with metal oxides such as Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, MgO, CaO, and Y\textsubscript{2}O\textsubscript{3} can produce stable molecules. Metal oxide will serve as a stabilizer that supports tetragonal structures to be more stable at room temperature, therefore more effective to inhibit crack propagation. When there is a stress application, a transition between the different crystal (reticulation) arrays due to force on the
zirconia surface occurs, resulting in a volumetric change in the crystal. This condition causes partially stabilized zirconia to have high strength and fracture toughness at the tip of the crack. The ability to inhibit the crack propagation is known as the transformation toughening mechanism [4-7].

To promote national independency, Indonesia researchers also encouraged to synthesize and fabricates filler components to develop dental materials products. Therefore, our research focusing on ZrO$_2$-Al$_2$O$_3$-SiO$_2$ synthesis as ceramic fillers to reinforces restorative dental materials, which compositional observations of morphological interest at a micron and sub-micron level features as well as to study the chemical composition of synthesized ZrO$_2$-Al$_2$O$_3$-SiO$_2$ ceramic fillers in terms of the amount of each element present characterized using Scanning Electron Microscopy (SEM) coupled with Spectrum-Line Energy Dispersive Spectroscopy (EDS). Those are two analysis techniques that are widely used to study morphology and elements of solid samples, from inorganic to biological [9].

2. Materials and Methods
2.1 Synthesis of ZrO$_2$-Al$_2$O$_3$-SiO$_2$
Zirconia-alumina-silica was synthesized using sol-gel technique. Aluminum nitrate nonahydrate [Al(NO$_3$)$_3$·9H$_2$O], tetraethyl orthosilicate (TEOS; Si(OCH$_2$)$_3$)$_4$, and zirconium chloride (ZrCl$_4$) were used as precursors. Distilled water and 1% w/v chitosan were used as solvent and dispersant, respectively. Briefly, 11.652 g of ZrCl$_4$, 9.378 g of Al$_2$NO$_3$ and 38.785 ml of TEOS were dissolved in 500 ml distilled water, followed by the addition of 100 ml of 1 w/v% chitosan solution. Subsequently, the solution was ultra-turaxed at 10 rpm for 5 minutes and repeated for 6 times. The as-prepared filler of composite was homogenized using ultrasonic homogenizer. After drying at 100°C, the filler particles of composite was calcined at 550°C for half an hour followed by calcined in 700°C for 2 hours in an electric furnace (Cress Electric Furnace C1228/935, Carson City, Nevada).

2.2 Characterization of ZrO$_2$-Al$_2$O$_3$-SiO$_2$
The as-synthesized powdered was characterized using Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). For EDS analysis, both spectrum point and line scanning were performed.

SEM as samples characterization technique can be used widely for hard materials, such as metals or ceramics, and soft materials, such as polymers or biological tissues. Electron beam is finely focused and scanned over the analysis area and signals are produced due to the electron-matter interactions on the surface of the specimen is the basic work principle of SEM. Such signals include secondary and backscattered electrons for the image formation and characteristic x-ray from the elements present in the sample for composition studies [9]. In order to evaluate the composition of the obtained ZrO$_2$-Al$_2$O$_3$-SiO$_2$ particles, EDS analysis was also performed. EDS analysis is a spectroscopic technique which allows to determine the presence and relative abundance of the elements that compose the surface of the specimen studied [9].

3. Results and Discussion
Figure 1 shows the SEM image of the ZrO$_2$-Al$_2$O$_3$-SiO$_2$ particles obtained by sol gel technique. The size of ZrO$_2$-Al$_2$O$_3$-SiO$_2$ particles measured by SEM ranges from 0.5 µm to 150 µm. The particles seem to be agglomerated. Based on the particle size the ZrO$_2$-Al$_2$O$_3$-SiO$_2$ filler can be classified as hybrid fillers.

Smaller filler particle size can increase the surface area, therefore surface smoothness and esthetics characteristic can be improved. A preliminary observation If the volume fraction of filler approximately 70%, abrasion and fracture resistance are raised to levels approaching those of tooth tissue, thereby increasing both clinical performance and durability. Ceramic fillers not only can be used for reinforcement materials, but also reduce polymerization shrinkage, reduction in thermal expansion, viscosity control, decreased water sorption, and imparting radio opacity [1, 10].

Sol gel technique used in this study is expected to produce ZrO$_2$-Al$_2$O$_3$-SiO$_2$ nanoparticles. However, nano-size particles could not be observed from SEM analysis. It is known that nanoparticles tend to agglomerate due to their high surface energy. Therefore, further experiments need to be carried out to grind down these agglomerated particles to nano-sized particles.
Figure 1. SEM image of the ZrO$_2$-Al$_2$O$_3$-SiO$_2$.

Figure 2. EDS analysis of ZrO$_2$-Al$_2$O$_3$-SiO$_2$ particles at 4 different points.

Figure 2 shows the relative amount of Zr, Al and Si elements in ZrO$_2$-Al$_2$O$_3$-SiO$_2$ particle at the given points in figure 1. The average amount of Zr, Si and Al elements is shown in table 1.

| Element | Value       |
|---------|-------------|
| Zr      | 34.65±7.09 wt% |
| Al      | 4.85±0.57 wt%  |
| C       | 18.17±0.57 wt%  |
| O       | 34.47±0.4 wt%  |
| Si      | 7.88±2.00 wt%  |

Table 1. Average amount of filler elements.

The EDS line scanning was also employed to evaluate whether the composition of Zr, Si, and Al is relatively similar throughout the particle. Figure 3 shows the EDS line scanning obtained from the ZrO$_2$-Al$_2$O$_3$-SiO$_2$ particles. EDS line scanning demonstrated that the composition of Zr, Si, and Al is relatively similar with that obtained in figure 2. The result indicated that the obtained particles have homogenous composition of Zr, Si, and Al.

The results of composition and morphological of ZrO$_2$-Al$_2$O$_3$-SiO$_2$ particles also can be influenced
by ceramic firing like the sintering temperature and time. The sintered particles would normally flow and fill up the pore spaces during sintering. Another study is being carried out to determine the relationship between sintering temperature/time and pore space generation. So far, a result from a porcelain version suggests that the sintering temperature may have distinguishable effects on pore generation [11].

Filler particles that incorporated to a resin matrix shall improve dental composite properties, which then provided well bond particles to a matrix. If not, the filler cannot provide reinforcement but will weaken the material [10].

Filler particles synthesized from zirconia as ceramic materials needs stabilization process to improve crack resistance as previously stated, so that the material can be applied to various kinds of prostheses. Zirconia can be stabilized as a whole (fully) or partially depending on the amount of stabilizer sufficient to form a particular crystalline phase. Partial stabilization involves the addition of
stabilizers such as Al₂O₃, SiO₂, CaO, MgO, La₂O₃ and Y₂O₃ in concentrations lower than those required for full stabilization resulting in cubic forms [4, 5, 10].

When stress occurs on the zirconia surface, the energy accumulated at the crack will cause the tetragonal crystal transition to become monoclinic and increase in volume. This crystal modification is followed by an expansion that can close existing cracks. The crystal transformation produces compressive stress as a result of volume expansion, thereby slowing down the propagation of the crack. This process is known as transformation toughening mechanism, which can ultimately improve the mechanical properties [4-6].

4. Conclusions
The ZrO₂-Al₂O₃-SiO₂ particles as dental composite fillers were successfully synthesized. Analyses using SEM demonstrated a heterogeneous grain size distribution ranges from 0.5–150 µm. The average composition of Zr, Si and Al in the obtained particle is 34.65±7.09 wt%, 7.88±2.00 wt%, and 4.85±0.57 wt% respectively. Based on the EDS line scanning, the obtained particles have homogenous composition of Zr, Si and Al. These results suggest that the samples provide good alternatives for ceramic fillers of dental composite.

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