ORIGINAL ARTICLE

The effect of $ZrCl_4$, $Al(NO_3)_3$ and Na_2SiO_3 precursors concentration on particle size as dental composites filler through spray pyrolysis method

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ABSTRACT

Introduction: one of the important components in dental composites is a filler which can be made through various methods, including spray pyrolysis. In the spray pyrolysis method, some factors determine the size and morphology of the resulting filler partides, one of which is the concentration of precursors. This study aimed to analyze the effect of precursor concentration on the particle size produced using the spray pyrolysis method. **Methods:** in this experimental laboratory study, zirconia-alumina-silica particles were synthesized using the spray pyrolysis method. The precursor solution consisted of $ZrCl_4$, $Al(NO_3)_3$, and Na_2SiO_3 with a concentration variation of (0.1; 0.2; and 0.3) M. The furnace temperature was set at 750°C, and the electric precipitator temperature was 100°C with a feed rate of 3L/min. Then, the tests performed were using PSA (Particle Size Analyzer), and XRF (X-Ray Fluorescence). **Results:** The results showed that the best zirconia alumina silica filler partide with the smallest size is the result with a concentration of 0.1 M and its size was 618.6 nm. The particle size for 0.2 M was 911.9 nm and 1799.4 nm for 0.3 M. According to XRF test results the zirconia alumina silica filler system contains all the precursor elements. **Conclusions:** The effect of precursor concentration on the particle size produced using the spray pyrolysis method showed that the smaller the precursor concentration used, the smaller the particle size produced. The best results from synthesizing a filler system with a concentration of 0.1 M precursor solution. All the results are in submicron and micron size, and could be used as the component of dental composites.

KEYWORDS

precursors concentration, particle size, spray pyrolysis, dental composites filler

INTRODUCTION

The dental composite was one of the widely used restoration materials in dentistry,[1] due to its superior aesthetic properties.[2] Indonesia was one of the countries that still imported dental composites from overseas, making it a relatively high cost for patients to treat their teeth problems. The availability of raw materials for synthesized dental composites in Indonesia made it possible to produce dental composites to reduce the mass dental treatment cost.

The dental composites contain three main components, i.e. matrix, filler, and coupling agent.[3] Among them, the filler has a significant role in determining the properties of dental composites. Materials that were commonly used as filler were zirconia (ZrO_2), alumina (Al_2O_3), and also silica (SiO_2).[4] Zirconia is a ceramic biomaterial frequently used in dentistry due to its biocompatibility and high strength.[5] Alumina has the same reason as zirconia for utility in dentistry, however, both have drawbacks in optical properties,[6] while silica has good optical properties.[7,8]

Many methods can be used to synthesize dental composite filler, such as geopolymerization, sol-gel, and spray pyrolysis. Further study showed that the geopolymerization method produced the particles in micron size.[9] To overcome the particle size, pyrolysis spray can be used. It produces particles in nano size according to many factors such as precursor's concentration, the temperature of the reactor or evaporation rate.[10]

Precursors used as the raw materials in the spray pyrolysis method can be one of the determinant factors for particle size being produced. One of the precursors for zirconia was zirconia chloride ($ZrCl_4$), for alumina was aluminum nitrate $Al(NO_3)_3$, and for silica was natrium silicate (Na_2SiO_3).

This research was conducted based on the two different statements related to precursor concentration using in spray pyrolysis method that two researchers have done. Jang et al.[11] stated that the precursors concentration affecting the particle size, the bigger the precursor's concentration, the bigger particle size will be produced. On the contrary, Denny et al.[12] said that the precursor's concentration, do not significantly affecting the particle size; depends on the temperature of the reactor. Regarding those statements, this study was conducted to verify which view can produce the smaller particle size. This study aimed to analyze the effect of precursor concentration on the partide size produced using the spray pyrolysis method.

METHODS

Zirconium chloride ($ZrCl_4$), aluminum nitrate ($Al,(NO_3)_3$) and natrium silicate (Na_2SiO_3) from Sigma-Aldrich were used as the precursor for synthesizing the filler system ZrO_2-Al_2O_3-SiO_2 with the aquadest as the solvent. There were two steps of procedures, i.e. synthesized filler system zirconia aluminasilica using spray pyrolysis method with precursor's concentration variation of (0.1; 0.2; 0.3) M and then characterized the particle has been produced using PSA (Particle Size Analyzer), and XRF (X-Ray Fluorescence). Firstly, dissolve 2.673 ml Na_2SiO_3 precursor in 100 ml aquadest to make sample A1 (0.1 M). Then mix with a magnetic stirrer for 10 minutes at 400 rpm stirring rate. Secondly, add 2.13-gram $Al(NO_3)_3$ precursor and stir for the same duration and rate. Lastly, pour 2.33 grams of ZrCl4 and stir for the same duration and rate. The final mix liquid must be homogenous without precipitate.

For samples A2 and A3 (0.2 and 0.3) M, the procedure slightly changes in method and duration for stirring $Al(NO_3)_3$. When $Al(NO_3)_3$ has been added, the mix becomes agglomerate and needs to be diluted by stirring manually using a glass rod. The duration of stirring using a magnetic stirrer for sample A2 was 15 minutes, and 20 minutes for sample A3. For mixing Na_2SiO_3 and $ZrCl_4$ precursors, use the same procedure as sample A1. The magnetic stirrer instrument we used can be seen in figure 1.

Figure 1. Magnetic stirrer, used for stirring

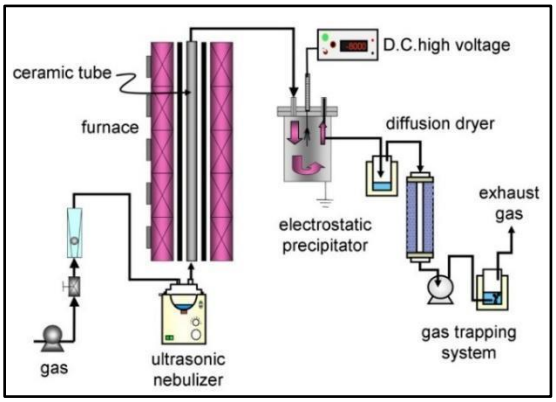

Figure 2. Scheme of spray pyrolysis instrument (Instrumentation system and functional material processing laboratory, Faculty of Physics Universitas Padjadjaran)

Put the homogenous mixture of precursors onto the ultrasonic nebulizer the set for a feed rate of 3 L/minute, 1.65 MHz piezoelectric and 750°C for the furnace temperature. The spray pyrolysis instrument can be seen in figure 2. The spray pyrolysis procedure begins when a nebulizer sprays the mixture of precursors into a droplet shape. Droplets that contain the solvent and precursor materials will be brought by a carrier gas into the reactor.

The reactor with high temperature evaporates the solvent, followed by a chemical reaction to form the particle. The particles that have been formed will be brought by the carrier gas and collected in an electric precipitator. This collector was a vessel with two high-voltage electrodes (about 10 kV). The particle can be taken out when all reach room temperature.

The collected particle is then characterized by PSA (Particle Size Analyzer), and XRF (X-Ray Fluorescence). The PSA measurements were analyzed using HORIBA SZ-100 for Windows [Z Type] Ver2. 20, and for XRF using NeX CG Rigaku.

RESULTS

Data were obtained for each variable of 0.1 M, 0.2 M, and 0.3 M, based on research carried out once with all conditions under control, including all tools and materials used and all procedures performed. The test results using the Particle Size Analyzer (PSA) on samples A1 (0.1 M), A2 (0.2 M), and A3 (0.3 M) showed that the particle distribution in one variety, namely monodisperse, seen from the PI (Polydispersity Index) value. The PI (Polydispersity Index) values obtained from each sample can be seen in table 1.

Table 1. Polydispersity Index values and particle size average of samples

Sample	PI (Polydispersity Index)	Particle size average (nm)
A1	0.484	618.6
A2	0.544	911.9
A3	0.544	1.799.4

Test results for particle size average of samples A1 (0.1 M), A2 (0.2 M) and A3 (0.3 M) using the Particle Size Analyzer (PSA) can be seen in table 1 and figure 3. The particle size average of sample A1 was 618.6 nm, A2 was 911.9 nm, and A3 was 1799.4 nm.

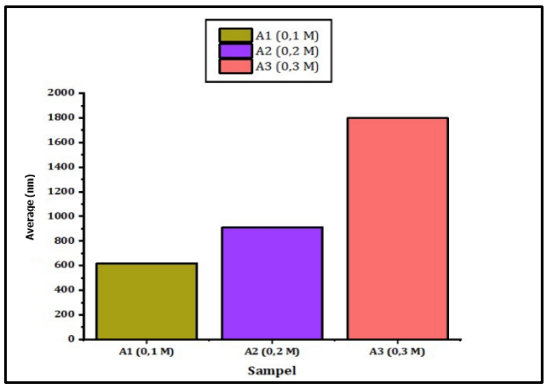

Figure 3. The particle size average of samples A1, A2 and A3 based on the results of the PSA measurement

A filler composition test of the zirconia alumina-silica system was also carried out using an X-Ray Fluorescence (XRF) test kit. The test results for samples A1, A2, and A3 can be seen in table 2. The XRF results show that the filler zirconia-alumina-silica system produced contains all the precursor elements used. The highest content was found in ZrO_2 particles, followed by SiO_2 and Al_2O_3.

Table 2. X-Ray Fluorescence test results for samples

Sample	Unit (%)		
	ZrO_2	Al_2O_3	SiO_2
A1	75.2	7.4	17.4
A2	84.6	5.13	10.3
A3	76.7	7.19	16.2

DISCUSSION

The results of the particle dispersion test for samples A1, A2, and A3, a homogeneous (monodisperse) solution pattern was obtained (Table 1), as characterized by a polydispersity index (PI) < 0.7 which is between 0.2–0.6 (< 0.7)[13,14,15] indicated that the particles were stable from the possibility of partide collision and gravity separation.

Synthesizing nano-sized filler particles, it was considered to use a modification of the precursor solution concentration to observe whether the resulting particles will be smaller when using low concentrations or vice versa. In the synthesis of this precursor solution, the concentration modification used was (0.1 M, 0.2 M & 0.3 M), as was done by Muchtar et al.[16] to study the effect of precursor concentration on manufacture ZnO using the spray pyrolysis method with the precursor concentrations used, namely (0.1 M-0.4 M). They stated that the concentration of the precursor is very influential to the particle size.

The spray pyrolysis method can produce spherical particles without aggregation and can produce in a short time.[17] The resulting particle size is controlled based on the concentration of the precursor used and the droplet size produced by the nebulizer. The droplet determines the conditions for evaporation, combustion, and the final result obtained.[18] Spray pyrolysis can control the partide structure in nano size.[19] By using filler in nano size (nanofiller), the filler volume can be further increased so that the mechanical properties and polishing ability will also increase.[7,20] However, in reality, it is difficult to control the morphology and size of the particles produced in the spray pyrolysis method due to sensitive factors such as the temperature at which the reaction occurs, the flow rate of the carrier gas, the precursor concentration and the power of the droplet-producing generator.[21]

The particle size produced in this study was not as expected in theory (in nanoparticles), namely below 100 nm. The results obtained were submicron in size (618.6 nm and 911.9 nm) and micron in size (1799.4 nm). This is also in accordance with research conducted by Cho, et al. which showed that the resulting particle sizes were submicron (280 nm, 630 nm) and micron (1100 nm and 1800 nm).[21] The discrepancy between theory and finding may be caused by factors such as the occurrence of coagulation when aerosols are formed, the presence of microporosity in the particles, and the occurrence of coalescence or agglomeration in the formed droplets.[18]

A Particle Size Analyzer (PSA) is a test tool that can be used to measure the size distribution of nanoparticles. PSA is considered a more accurate method compared to SEM or TEM tests because it uses laser light as a medium for measuring test samples (particles).[22] In sample A1, the results showed an average size of 618.6 nm, sample A2 an average size of 911.9 nm, and sample A3 an average size of 1799.4 nm. The order of the average diameter from largest to smallest is sample A1 followed by samples A2 and A3. This difference in average size can occur due to different concentrations of precursor solutions. The difference can be affected too by the process during synthesis. The droplets from the nebulizer are brought to the reactor and undergo an evaporation process due to heating. This evaporation causes the process of precipitation of the solute in the droplet to increase beyond its solubility limit. At high concentrations, the process of precipitation of solutes in droplets takes place faster so that the time is relatively short for forming particles with larger sizes compared to those produced at low concentrations.[16] However, in this study, the particle size synthesized was not close to the standard value of nanoparticles, namely 1-100 nm.

Another characteristic test carried out is X-Ray Fluorescence (XRF). This characteristic test determines the content of resulting particles based on identifying elements that make up a particle. This test tool has the advantage of uncomplicated sample preparation and does not damage the test sample.[23] In this study, the zirconia alumina-silica system filler produced was subjected to XRF testing. It contained all precursor components after being synthesized using the spray pyrolysis method. However, from the test results, the percentage of ZrO_2 is substantial compared to Al_2O_3 and SiO_2.

The limitations of this study were in the tools and materials used, which then affected the time needed. One of the tools used, namely, pyrolysis spray, is limited in number, so it often takes quite a long time to get the required data. In addition, one of the materials used is rather difficult to handle, so it requires high precision to get optimal results. To overcome this, it is recommended that the required tools be provided in sufficient quantities, and the handling of materials must be done carefully to get the expected results.

CONCLUSION

The effect of precursor concentration on the particle size produced using the spray pyrolysis method showed that the smaller the precursor concentration used, the smaller the particle size produced. The best results from synthesizing a filler system with a concentration of 0.1 M precursor solution. All the results are in submicron and micron size, and could be used as the component of dental composites.

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Data Availability Statement: data supporting reported results can be found, including links to publicly archived datasets analyzed or generated during the study.
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