Preparation of Spherical Silica Based-Fillers with Zirconia for Dental Composite by Spray Pyrolysis

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Abstract

SiO₂-Y₂O₃ stabilized ZrO₂ (YSZ) nano-hybrid fillers were successfully prepared by spray pyrolysis process. The chemical and physical properties of SiO₂-YSZ nano-hybrid fillers were characterized by powder X-ray diffraction (XRD), a field-emission scanning electron microscope (FE-SEM), and a transmission electron microscopy (TEM) using energy dispersive X-ray spectrometer (EDS). XRD revealed that the crystal phases of SiO₂-YSZ nano-hybrid fillers were the phases of both amorphous SiO₂ and tetragonal YSZ. SiO₂-YSZ nano-hybrid fillers exhibited spherical morphology with approximately 1 μm. The flexural strengths of the dental composites as the property of filler were examined. The difference in the primary particle size of SiO₂-YSZ nano-hybrid fillers was related to the difference in the flexural strengths. The SiO₂-YSZ nano-hybrid fillers formed by the primary particles with approximately 90 nm exhibited high flexural strength of the dental composites. The flexural strength of the dental composites using that SiO₂-YSZ nano-hybrid fillers formed by the primary particles with approximately 90 nm was approximately 210 MPa.

Keywords: Composite filler, Dental composite, CAD/CAM resin, Spray pyrolysis, Filler.

1. Introduction

The resin composites have been widely used as dental filling materials¹⁾. However, flexural strength, compressive strength, and wear resistance of the resin composites are low for using with canines and posterior teeth¹⁻³⁾. Dental resin composites (dental composites) mainly consist of resin matrix and oxide fillers. The powder characteristics of oxide fillers contribute significantly to mechanical property such

as the flexural strength. The flexural strength of front teeth is approximately 100 MPa. On the other hand, the flexural strengths of canines and posterior teeth range from approximately 200 to 500 MPa. SiO₂ based-particles with Al₂O₃, ZrO₂, TiO₂, and CaO either alone or in combination have been usually used as fillers¹⁾. The flexural strengths of SiO₂ and Al₂O₃ ceramics is approximately 120 MPa, respectively. Therefore, the flexural strengths of dental composites with SiO₂ based-fillers with Al₂O₃ are lower than 120 MPa. It is known that the using of ZrO₂ to SiO₂ based-fillers is effective for improvement of mechanical properties of the dental composites⁴⁻⁶⁾. The flexural strength and compressive strength of ZrO₂ ceramics with tetragonal and cubic structure are higher performance than that of ZrO₂ ceramics with monoclinic structure. The crystal phase of ZrO₂ is monoclinic structure at room temperature. Tetragonal and cubic phases can be stabilized upon doping with trivalent ions such as Y³⁺^{7, 8)}.

Spray pyrolysis is a versatile process that is used to synthesize fine oxide particles and fine metal particles⁹⁾. Spray pyrolysis can convert a droplet of the starting solution into an oxide or metal particle at one step, and is a continuous process. The advantages of spray pyrolysis are that it allows to control of the particle size, particle size distribution, and particle morphology. In addition, fine particles with a homogeneous composition can be easily synthesized, because the starting solution components are kept in a droplet. The features of spray pyrolysis that can produce fine particles in one step and continuously is a great advantage for industrial powder production.

In this study, it tried to prepare SiO₂-Y₂O₃ stabilized ZrO₂ (YSZ) nano-hybrid fillers by spray pyrolysis in order to improve the flexural strength of the dental composites. The effect of starting materials and the surface micro-

structures of particle on the flexural strength of the dental composites was investigated. The particle characteristics were also investigated.

2. Experimental procedure

2.1 Preparation of the oxide fillers

Spray pyrolysis⁽⁹⁾ was used to prepare SiO₂-YSZ particles. Si(OC₂H₅)₄ (TEOS) and three types of SiO₂ sols were used as a silicon source. Average particle sizes of these SiO₂ sols were 15, 35, and 95 nm, respectively. ZrO(NO₃)₂·2H₂O and Y(NO₃)₃·6H₂O were used as the starting materials for YSZ. ZrO(NO₃)₂·2H₂O and Y(NO₃)₃·6H₂O were dissolved in the solution of SiO₂ sols at room temperature. The molar ratio of the metal component (Si:Zr) was set to 3:1 in the solution. The molar ratio of the metal component (Zr:Y) was set to 97:3 in the solution. The concentration of the starting solutions was 0.1 mol/dm³. The starting solutions were converted to mists using an ultrasonic nebulizer. Air was used as the carrier gas during the preparation of SiO₂-YSZ particles. The generated mists were carried to an alumina tube that was heated by two electric furnaces, and then pyrolyzed. The flow rate of the carrier gas was 7 dm³/min. The temperature of an electric furnace in the drying zone were 400 °C. The temperature of an electric furnace in the pyrolysis zone were 800 °C. The precursor particles were continuously collected using a cyclone system. Furthermore, the precursor particles were calcined from 800 to 1100 °C for 2 h in an electric furnace under an air atmosphere in order to investigate the effect of the calcination temperature on the particle characteristics. A silane coupling agent was used to enhance the interfacial interactions between the resin matrix and the calcined particles. 3-methacryloxypropyl trimethoxysilane (3-MPS) was used as a silane coupling agent. 3-MPS has been adopted as an industry standard coupling agent⁽¹⁾. The surface-modified particles were used as fillers.

2.2 Characterization of the particles

The crystal phase of the obtained particles was identified by powder X-ray diffraction (XRD, Rigaku, Mini Flex II) using Cu K α radiation. The particle size and morphology of the obtained particles were determined by using a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-7610F). In the FE-SEM images, 200 particles were randomly sampled to determine the average particle size. Chemical analysis of the calcined particles was carried out a

transmission electron microscopy (TEM, JEOL, JEM-2100) using energy dispersive X-ray spectrometer (EDS, JEOL, JED-2300T).

2.3 Preparation of the dental composites

The dental composites were prepared in order to examine the flexural strength of the dental composites used the prepared fillers. The monomer urethane dimethylacrylate (UDMA, Sigma-Aldrich) was manually mixed to the monomer triethylene glycoldimethacrylate (TEGDMA, Sigma-Aldrich). The weight ratio of the monomer component (TEGDMA:UDMA) was set to 70:30. For the polymerization, 0.5 wt% camphorquinone (Sigma-Aldrich) as photo initiator was added. These monomers and camphorquinone were manually mixed in the dark, during 30 min. The fillers were manually blended with the monomers mixture by using a mortar and pestle, until obtaining a homogeneous paste, in the dark.

2.4 Flexural tests of the dental composites

The specimens (25 mm × 2 mm × 2 mm) for the flexural tests were prepared by filling a stainless steel split mold with uncured dental composites, following the ISO 10477. Then, the specimens were photo-cured by applying light (375–495 nm) for 60 s. The flexural strength of the specimens was measured using a three-point bending test. All tests were carried out at a cross-head speed of 1.0 ± 0.3 mm/min until fracture occurred. The load was applied to the center of the specimens placed on supports with 20 mm span. The flexural strength (σ) was calculated by the following equations:

$$\sigma = \frac{3Fl}{2bh^2} \quad (1)$$

where F is the maximum load exerted at the fracture point, l is support span length, b and h are the width and height of the specimen measured prior to test.

3. Results and discussion

3.1 Particle characteristics

The effect of changing the calcination temperature on the crystal phases of the obtained particles was investigated. The calcination temperatures were from 800 to 1100 °C. The crystal phases of the obtained particles were observed by using the XRD. Figure 1 shows the XRD patterns of the precursor particles obtained from the SiO₂ sol with 95 nm.

Fig. 1. XRD patterns of the precursor particles obtained from the SiO₂ sol with 95 nm.

Fig. 2. XRD patterns of the precursor particles and calcined particles that obtained from the SiO₂ sol with 95 nm.

The broad halo due to amorphous SiO₂ was observed at 20–30°. The other diffraction patterns were agreement with the diffraction patterns of tetragonal ZrO₂, and the other phases such as ZrO(NO₃)₂·2H₂O, Y(NO₃)₃·6H₂O, and monoclinic phase were not observed. The crystal phase of ZrO₂ is monoclinic structure at room temperature. Therefore, the doping of yttrium led to stabilization of tetragonal structure at room temperature^(7, 8). Figure 2 shows the XRD patterns of

Fig. 3. FE-SEM images of the precursor particles and the calcined particles that obtained from the SiO₂ sol with 95 nm.

the precursor particles and the calcined particles that obtained from the SiO₂ sol with 95 nm. The crystal phases of the calcined particles were that of amorphous SiO₂ and tetragonal ZrO₂, and the other phases were not observed. This suggested that the composite particles of SiO₂ and YSZ were obtained. The crystallinity of YSZ phase became high with increasing calcination temperature. Regardless of the type of silicon source as starting material, the crystal phases of the calcined particles that obtained from TEOS and the SiO₂ sols (15, 35 nm) were also that of amorphous SiO₂ and tetragonal ZrO₂.

Figure 3 shows the FE-SEM images of the precursor particles and SiO₂-YSZ particles calcined at 1100 °C that obtained from the SiO₂ sol with 95 nm. The precursor particles and SiO₂-YSZ particles calcined at 1100 °C were spherical particles and non-aggregated. When the SiO₂ sol with 95 nm were used as a silicon source, the primary particles with approximately 90 nm aggregated and the spherical secondary particles were formed, regardless of the calcination temperature. It was found that the changing the calcination temperature do not effect on the surface morphology of the calcined particles when the calcination temperature ranged from 800 to 1100 °C.

Figure 4 shows the FE-SEM images of SiO₂-YSZ particles calcined at 1100 °C, when TEOS and three types of SiO₂ sols (15, 35, and 95 nm) were used as a silicon source. SiO₂-YSZ particles calcined at 1100 °C exhibited spherical morphology with approximately 1 μm, regardless of the type of silicon source. When the SiO₂ sols were used as a silicon source, the primary particles aggregated and the spherical secondary particles were formed. The primary particle sizes of SiO₂-YSZ particles obtained from the SiO₂ sols was almost the same as the particle sizes of the SiO₂ sols used as a silicon source.

Fig. 4. FE-SEM images of SiO₂-YSZ particles calcined at 1100 °C.

Figure 5 shows the scanning TEM (STEM) image of SiO₂-YSZ secondary particle calcined at 1100 °C that obtained from the SiO₂ sol with 95 nm, and also STEM-EDS elemental mapping of SiO₂-YSZ particles. This analysis elucidates the selective Si and Zr segregation within the particles. Si was distributed inside the primary particles. On the other hand, Zr was distributed on the surface of the primary particles. This suggested that the spherical secondary particles were formed by SiO₂-YSZ primary particles with nano-sized.

3.2 Flexural property of the dental composites

The flexural strengths of the dental composites as the property of filler were examined. Figure 6 shows the flexural strengths of the dental composites. SiO₂-YSZ particles calcined at 1100 °C were used as fillers. SiO₂-YSZ particles calcined at 1100 °C were surface-modified by a silane coupling agent (3-MPS). In order to allow a high particle packing (> 60 wt%) to the monomers, SiO₂-YSZ surface-modified nanoparticles with approximately 90 nm were also used as fillers^(2, 10 11). SiO₂-YSZ surface-modified nanoparticles was blended with SiO₂-YSZ surface-modified particles calcined at 1100 °C. The weight ratio of the filler component (SiO₂-YSZ surface-modified particles:SiO₂-YSZ surface-modified nanoparticles) was set to 70:30. The total filler contents were 79 wt% in each the dental composites, respectively. When SiO₂-YSZ surface-modified particles

Fig. 5. (a) STEM image of SiO₂-YSZ secondary particle calcined at 1100 °C that obtained from the SiO₂ sol with 95 nm. (b) STEM image, and corresponding STEM-EDS maps elucidating the distribution of Si, Zr, Si and Zr over the area within the frame in Fig. 5(a).

Fig. 6. Flexural strengths of the dental composite. The calcined particles obtained from (a) TEOS, (b) SiO₂ Sol with 15 nm, (c) SiO₂ Sol with 35 nm, and (d) SiO₂ Sol with 95 nm were used as fillers.

obtained from TEOS and the SiO₂ sol with 15 nm were used as fillers, the flexural strengths of the dental composites were both approximately 160 MPa. When SiO₂-YSZ surface-

modified particles obtained from the SiO₂ sol with 35 nm were used as filler, the flexural strengths of the dental composites increased to approximately 170 MPa. Furthermore, the flexural strengths of the dental composites increased to approximately 210 MPa, when SiO₂-YSZ surface-modified particles obtained from the SiO₂ sol with 95 nm were used as filler. It was found that the flexural strengths of the dental composites increased as the primary particle size of fillers increased. It is considered that the surface roughness of SiO₂-YSZ particles contributed to the strength of the anchoring effect at the interface between fillers and resin, and this resulted in increasing flexural strengths.

4. Conclusions

SiO₂-YSZ spherical particles were successfully prepared by spray pyrolysis process. SiO₂-YSZ spherical particles were the secondary particles with approximately 1 µm formed by SiO₂-YSZ primary particles and were nonaggregated. The calcination temperature between 800 and 1100°C influenced the crystallinity and did not the surface microstructure of particle. XRD revealed that the homogeneous crystal phase of SiO₂-tetragonal YSZ obtained by calcining from 800 to 1100°C. XRD, FE-SEM observation, and EDS analysis indicated that SiO₂-YSZ particles had a hybrid structure by SiO₂ and YSZ at a nano-order. The difference in the primary particle size of SiO₂-YSZ fillers influenced the flexural strengths of the dental composites. The flexural strengths of the dental composites using SiO₂-YSZ fillers increased from 160 MPa to 210 MPa as the primary particle size of fillers increased from approximately 10 nm or less than to approximately 90 nm.

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