Fabrication of Nearly Monodispersed Silica Nanoparticles by Using Poly(1-vinyl-2-pyrrolidinone) and Their Application to the Preparation of Nanocomposites

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Abstract: To fabricate dental nanocomposites containing finely dispersed silica nanoparticles, nearly monodispersed silica nanoparticles smaller than 25 nm were synthesized without forming any aggregates via a modified sol-gel process. Since silica nanoparticles synthesized by the Stober method formed aggregates when the particle size is smaller than 25 nm, the synthetic method was modified by changing the reaction temperature and adding poly(1-vinyl-2-pyrrolidinone) (PVP) to the reaction mixture. The size of the formed silica nanoparticles was reduced by increasing the reaction temperature or adding PVP. Furthermore, the formation of aggregates with primary silica nanoparticles smaller than 25 nm was prevented by increasing the amount of PVP added to the reaction mixture. To enhance the dispersion of the silica particles in an organic matrix, the synthesized silica nanoparticles were treated with 3-methacryloxypropyltrimethoxysilane (γ-MPS). A dental nanocomposite containing finely dispersed silica nanoparticles could be produced by using the surface-treated silica nanoparticles.

Keywords: silica nanoparticles, aggregates, PVP, surface treatment, nanocomposite.

Introduction

Over the past several decades, there has been rapidly increasing interest in the preparation of nanometer-sized materials such as nanoparticles, nanowires, and superlattices.[1-4] Among these, silica nanoparticles are widely used in various fields including ceramics, chromatography, catalysis, and chemical mechanical polishing.[5-8] Additionally, precursor silica particles have been used in stabilizers, coatings, glazes, emulsifiers, strengtheners, and binders. The need for well-defined silica nanoparticles has increased in high-tech industries such as biotechnology and pharmaceuticals.

Since commercial introduction of polymeric dental restorative composites in the mid-1960s, they are widely used instead of amalgam because composites make up for the weak points of amalgam, such as toxicity from mercury content, corrosion, low adhesive property, and poor aesthetic property.[9-13] The scope of their applications has expanded continuously from small anterior restorations to large posterior restorations and even fixed partial dentures. Dental composites mainly consist of inorganic fillers and an organic matrix. Widespread dental composites mainly consist of an organic matrix and inorganic fillers, i.e., micron-size particles (microfillers).[14-24]

Comparing properties of dental composites with those of amalgam, they have a disadvantage in wear resistance and long-term service. Recently, to overcome disadvantages of the dental composites containing microfillers, dental nanocomposites were introduced by incorporating a hybrid concept compounding with sub-100 nanoparticles.[21-24] Dental nanocomposites are theoretically purported to have increased wear and fatigue resistance as compared with microfill composites and may favor the achievement of restoratives with better long-term performance. Studies related to the effects of filler size on wear exhibited that a finer particle size for the composite results in less interparticle spacing, more protection of the softer resin matrix, and less filler plucking, all of which lead to enhanced wear resistance for the material.[16-22] These studies were, however, performed on microfillers rather than nanofillers. On the basis of the promising potential of nanocomposites, wear and fatigue resistance of commercial dental nanocomposites were explored previously.[21-24] However, the results indicated that the commercial dental nanocomposites were not likely to provide improved wear and fatigue performance over the traditional microfill composites because they contain the aggregates with primary silica nanoparticles. To understand the relationship between nanofiller size, wear, and fatigue resistance of the dental composite, nanocomposites containing uniform sized nanofillers should be prepared. In the previous studies, to prepare nearly monodispersed silica nanoparticles having different sizes via a sol-gel process,

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contents of reactants, catalyst in the reaction mixture, reaction temperature, solvent, and reaction medium were varied.[25-36] The decline in the particle size was observed by decreasing TEOS and NH_4OH concentration and by increasing water concentration.[25-31] Several studies revealed that the particle size can be reduced by increasing reaction temperature, and the use of methanol instead of ethanol also reduces particle size.[31-34] Ultrasonication during reaction and changes in the reaction medium such as addition of seed sol or surfactant also affect on the particle size and aggregates formation.[35,36] Such modifications in the sol-gel process were somewhat successful in producing nearly monodispersed silica nanoparticles but have the drawbacks such as formation of aggregates and a poor-spherical shape. Fabrication of nearly monodispersed silica nanoparticles smaller than about 25 nm without aggregates formation is still under studying, even though nearly monodispersed nanoparticles larger than about 25 nm can be obtained by varying reaction conditions.

To fabricate nearly monodispersed silica nanoparticles smaller than about 25 nm by preventing aggregates formation, solvent, the reaction temperature, and reaction medium were changed in this study. The surface of the synthesized silica nanoparticles was treated with 3-methacryloxypropyl-trimethoxysilane (γ-MPS) to improve dispersion of nanofillers to the resin matrix and then the morphology of the dental composites containing silica nanoparticles synthesized here was observed with field emission scanning electron microscopy (FE-SEM). The issues related to the effects of nanofiller size on the wear and fatigue resistance will be the topic of a forthcoming paper.

Experimental

Materials. A sol-gel reaction, i.e., Stöber method was facilitated by hydrolysis and condensation of tetraethylorthosilicate (TEOS, 98+%, Aldrich Chemical Co., USA) and deionized water in a solvent with a base catalyst.[25-33] Reagent grade ammonium hydroxide (30% NH_4OH Samchun Pure Chemical Co., Korea) was used as the base catalyst. Absolute methanol, ethanol, or isopropanol purchased from Aldrich Chemical was used as a solvent. Poly(1-vinyl-2-pyrrolidone) (PVP) having various molecular weights ($\overline{M}_w$ = 10,000, $\overline{M}_w$ = 55,000, $\overline{M}_w$ = 360,000, $\overline{M}_w$ = 1,300,000) were also purchased from Aldrich Chemical. 3-Methacryloxypropyl-trimethoxysilane (γ-MPS, 98%, Aldrich Chemical Co.) was used as the silane coupling agent for hydrophobic treatment of the filler. 2,2-Bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (Bis-GMA, Polysciences Inc.) as a base resin, triethylene glycol dimethacrylate (TEGDMA, Aldrich Chemical Co.) as a diluent, camphorquinone (CQ, 99%, Aldrich Chemical Co.) as an initiator, and ethyl 4-dimethylaminobenzoate (EDMAB, 99+%, Aldrich Chemical Co.) as an accelerator were used.

Procedures. Silica particles having different size were prepared by a modified Stöber method. It is known that silica nanoparticles (average diameter: 50 nm) is formed when reaction is performed with methanol (1 L) solution containing TEOS (0.28 mol), water (20 mol), NH_4OH (2 mol) at 30 °C for 1 h.[26] To understand the effects of kind of solvent and reaction temperature on the synthesized particles size, silica nanoparticles were synthesized with various solvents such as methanol, ethanol, or isopropanol at various reaction temperatures when composition of reaction mixture was fixed. PVP was added to the reaction mixture to prevent the formation of the aggregates with primary silica nanoparticles. For the synthesis, solvent, ammonium hydroxide and deionized water were first mixed and then TEOS was added. The reaction was performed at various temperatures for 1 h and then the resulting product was centrifuged at 20,000 rpm for 1 h by using ultracentrifuge (model:T-1180, Kontron, Italy). The obtained silica particles were washed with deionized water after isopropyl alcohol (IPA) washing to remove unreacted TEOS. Finally, silica particles were dried in an air circulating oven at 110 °C for 24 h.

The hydrophilic surface of the synthesized nanofiller caused by hydroxyl end groups was treated with the γ-MPS to improve dispersion of nanofiller in an organic matrix as described previously.[25,37,38] γ-MPS was pre-hydrolyzed by reacting with deionized distilled water and ammonium hydroxide at 30 °C for 2 h. Silica nanofillers was continuously added to the γ-MPS solution and stirred at 1,000 rpm for 2 h. After removing unreacted γ-MPS by using an ultracentrifuge, the resulting product was further purified by freeze-drying at -50 °C for 2 days. The surface treated filler was finally cured at 120 °C for 2 h to accomplish condensation reaction.

Organic matrix containing 70 wt% of Bis-GMA as a base resin and 30 wt% of TEGDMA as a diluent was used to prepare dental composites.[10-16] Even though dental composites generally contains more than 70 wt% of inorganic filler, nanocomposites containing 10 wt% silica nanoparticles were prepared to observe the dispersion of the nanofillers in the organic matrix. Mixing of the organic matrix and nanofillers was performed in a twin extruder (Bau Tech, model: BA-11, L/D ratio = 40, Korea) at 30 °C. The dental composites were placed in a DSC (differential scanning calorimeter, TA Instruments, TA-2100, USA) sample pan (6 mm diameter × 2 mm thickness) and polymerized by irradiating with visible light from a light source (λ_{max} 460 nm, intensity 600 mW/cm^2, VIP™ Junior Curing Light, BISCO Inc., USA) under a nitrogen-purged condition.

The morphologies of the synthesized silica nanoparticles were observed with Transmission Electron Microscopy (TEM, model: JEM 2000EXII, JEOL, Japan). Average size of silica nanoparticles was determined from TEM images. Ten TEM images were obtained from ten different specimens for each sample and then an image analysis software (BMI Series ver. 4.0, Korea) was used to obtain average particle size. To

investigate changes in the dispersion of silica nanofiller, cured dental composites were fractured in liquid nitrogen condition and then the morphology of the fracture surface was observed with FE-SEM (Field Emission Scanning Electron Microscope, JSM-6700F, JEOL, Japan).

Results and Discussion

Size Changes of Silica Nanoparticles. The size of silica particles synthesized by the Stöber method depends on amount of reactants (water and TEOS) and catalyst (ammonium hydroxide).[25-31] The decline in the particle size was observed by decreasing TEOS and NH₄OH concentration and by increasing water concentration, and silica nanoparticles having various sizes from 5 to 50 nm was synthesized when methanol was used as a solvent. Nearly monodispersed nanoparticles were formed when particles size was larger than 25 nm, while aggregates formed with primary silica nanoparticles start to form when their size was below about 25 nm. To prevent the formation of the aggregates, the kind of solvent, the reaction temperature, and reaction medium were changed in this study.

To understand the effects of the kind of solvent on the particles size, silica nanoparticles were synthesized by using various solvents (methanol, ethanol, isopropanol) when composition of reaction mixture and reaction temperature were fixed. The particles size was reduced in the order of isopropanol (250 nm), ethanol (125 nm), and methanol (5 nm) as shown in Figure 1. Note that the trends related to the particle size changes with the kind of solvent were not changed regardless of the compositions of the reaction mixtures. Changes in the particle size with the solvent used for the synthesis of silica particles stemmed from the differences in the size of nuclei formed in each solvent. Since the supersaturation ratio of the hydrolyzed monomer in the solvent is decreased by increasing the molecular weight of solvent, the nuclei created in the solvent having low molecular weight are smaller than those created in the solvent having high molecular weight.[31-33] Because of this, silica nanoparticles synthesized by using methanol as a solvent have the smallest particles size.

Changes in the particles size with reaction temperature was examined when the composition of the reaction mixture and the kind of solvent were fixed. Figure 2 exhibits changes in particles size with reaction temperature when ethanol was used as solvent. Note that silica nanoparticles having average diameter of 45 nm were formed when reaction was performed at 30 °C with the reaction mixture composed of TEOS (0.28 mol), water (20 mol), NH₄OH (0.5 mol), and ethanol (1 L). The particles size was decreased by increasing reaction temperature and then leveled off to a fixed value. The size of the nearly monodispersed silica nanoparticles prepared at the reaction temperature of 30 °C (45 nm) was decreased to the size of about 5 nm when reaction tem-
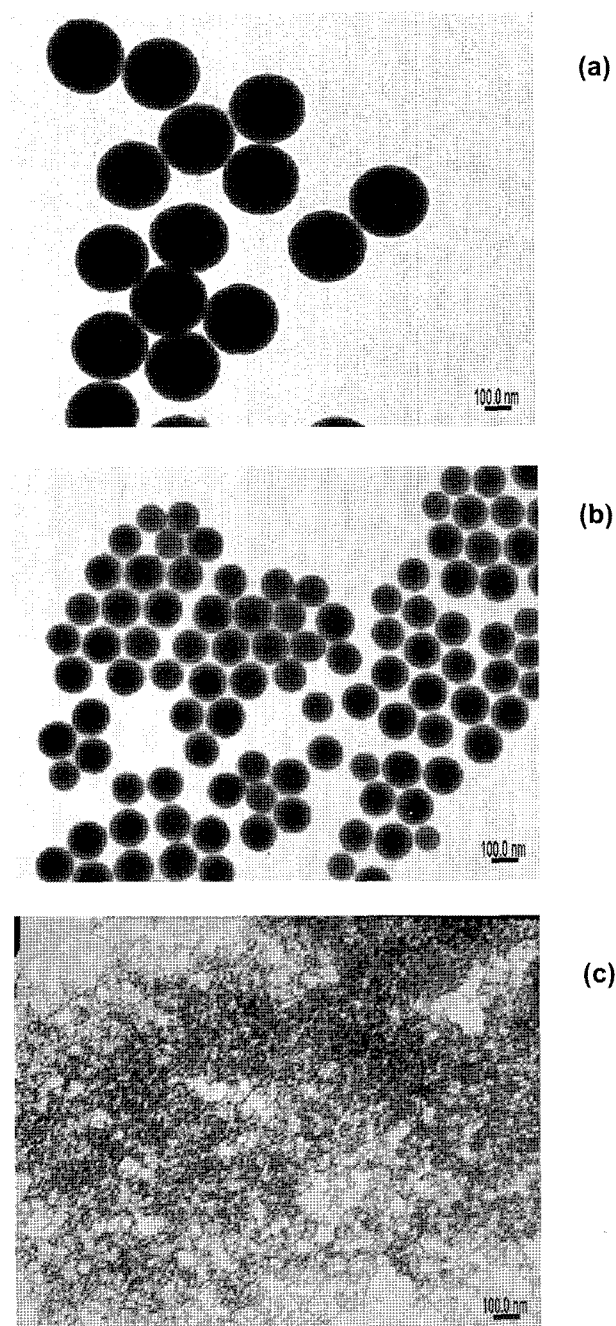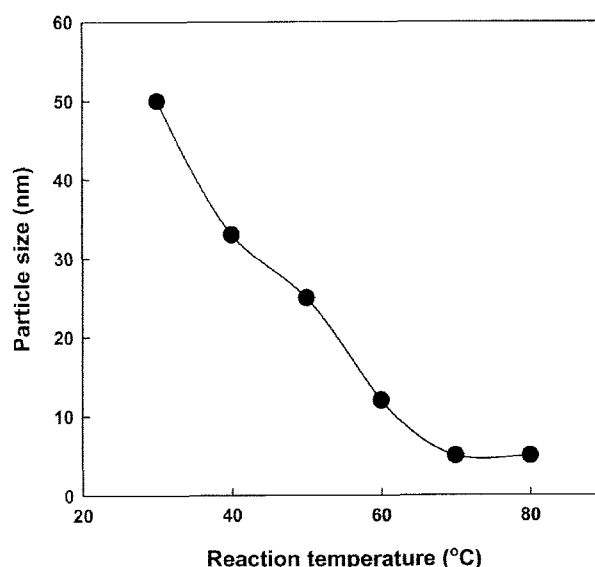

Figure 1. TEM microphotographs exhibiting the effects of solvent changes on the silica particles size. Note that reaction mixture was composed of TEOS (0.28 mol), water (10 mol), NH₄OH (0.5 mol), and solvent (1L) and reaction temperature was fixed at 30 °C: (a) isopropanol (250 nm), (b) ethanol (125 nm), and (c) methanol (5 nm).
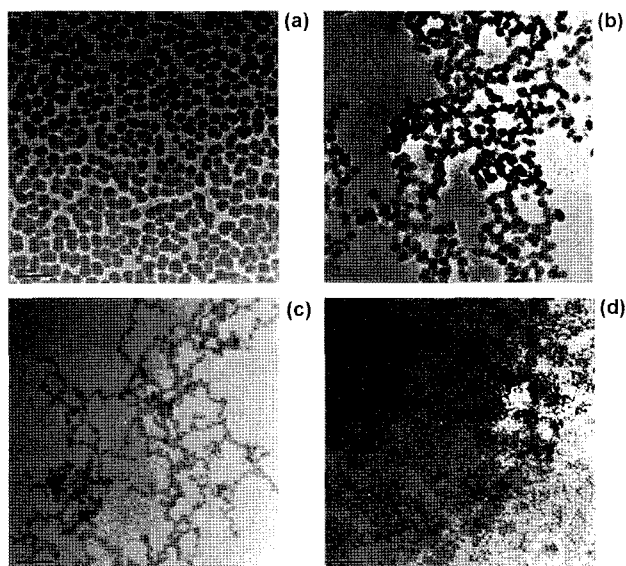
perature was higher than or equal to 80 °C. It was known that the reaction temperature effects related to the saturation concentration of ammonia, which decreased with increasing temperature.[31,39] A decrease in the saturation concentration of ammonia with temperature reduces particle size. Nearly monodispersed nanoparticles were formed when particles
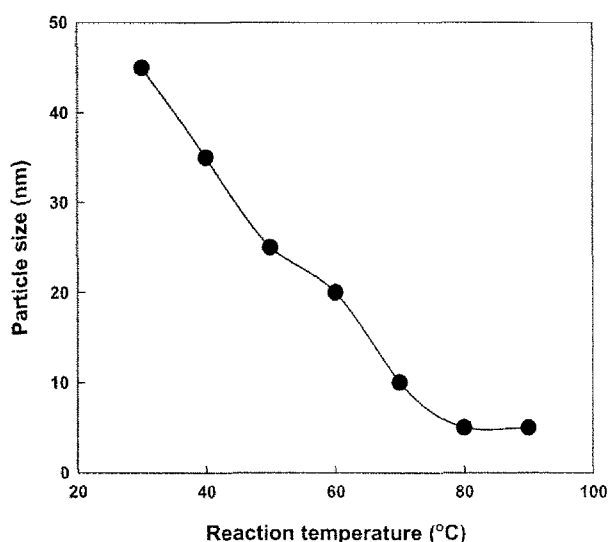
Figure 2. Changes in particles size with reaction temperature when ethanol was used as solvent. Note that silica nanoparticles (45 nm) were formed when reaction was performed at 30 °C with the reaction mixture composed of TEOS (0.28 mol), water (20 mol), NH$_4$OH (0.5 mol), and ethanol (1 L).


Figure 3. TEM microphotographs of the silica nanoparticles synthesized at various reaction temperatures by using ethanol as a solvent; (a) 50 °C (25 nm), (b) 60 °C (20 nm), (c) 70 °C (10 nm), and (d) 80 °C (5 nm).

size was larger than or equal to about 25 nm as shown Figure 3. However, aggregates with primary silica nanoparticles start to form when their size was below about 20 nm. These results might be stemmed from following reasons. The smaller particles formed, the more particles produced. Since small particles have higher surface tension than large particles, they easily aggregate to make their surface to be more stable. Because of these, primary silica particles,

Figure 4. Changes in particles size with reaction temperature when methanol was used as solvent. Note that silica nanoparticles (50 nm) were formed when reaction was performed at 30 °C with the reaction mixture composed of TEOS (0.28 mol), water (10 mol), NH$_4$OH (2 mol), and methanol (1 L).

whose size is below about 20 nm, start to form aggregates while spherical particles were formed without aggregation when their size was larger than or equal to about 25 nm. Figure 4 showed that the particles size was also decreased by increasing reaction temperature and then leveled off to a fixed value when methanol was used as solvent. The formation of aggregates examined with methanol solvent was also exhibits the same trends with that examined with ethanol. The results obtained here indicated that the size of silica nanoparticles could be controlled by changing reaction temperature and solvent, but problems related to the aggregate formation could not be solved by changing reaction temperature or solvent.

To fabricate nearly monodispersed silica nanoparticles without aggregate formation, PVP was added to the reaction mixture. The addition of PVP, which is soluble in water and various alcohols such as methanol, ethanol, and isopropanol, increases the viscosity of reaction mixture. Changes in the viscosity of medium may affect the size of nuclei formed in a solvent and the growth rate of nuclei because the diffusion rate of reactants to the nuclei may be retarded. Figure 5 shows changes of particles size when PVPs (30 g) having various molecular weights were added to the reaction mixture and methanol was used as a solvent. The solution viscosity increases with molecular weight of PVP when the same amount of PVP is dissolved. The particles size was gradually decreased by increasing the molecular weight of PVP and then leveled off a fixed value. This result indicates that the particles size can be reduced further by controlling
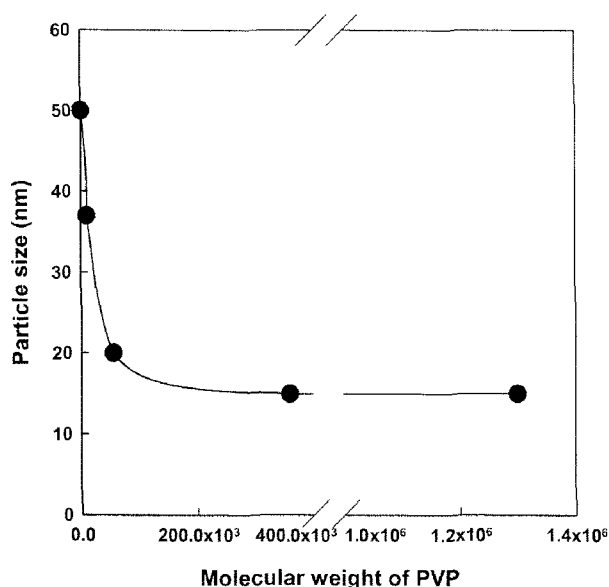
Figure 5. Changes of particles size when PVPs (20 g) having various molecular weights were added to the reaction mixture and methanol was used as a solvent. Note that silica nanoparticles (50 nm) were formed without addition of PVP when reaction was performed at 30 °C with the reaction mixture composed of TEOS (0.28 mol), water (10 mol), NH₄OH (2 mol), and methanol (1 L).
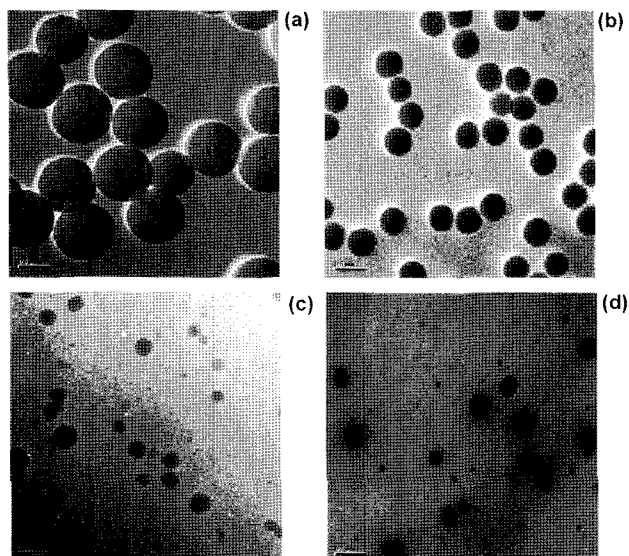

Figure 6. Morphology changes of silica particles observed with TEM when 30 g of PVPs having various molecular weights were added to the reaction mixtures; (a) without PVP, (b) PVP ($\overline{M}_w$ = 10,000), (c) PVP ($\overline{M}_w$ = 55,000), and (d) PVP ($\overline{M}_w$ = 360,000).

the viscosity of reaction mixture. The aggregates with primary silica nanoparticles were still formed when the size of the formed primary particles smaller than about 20 nm.

PVPs having various molecular weights were also added reaction mixture containing isopropanol as a solvent. Note that nearly monodispersed silica particles having about 900

nm diameter were formed without PVP addition to the reaction mixture (Figure 6(a)). Nearly monodispersed silica nanoparticles (about 450 nm, Figure 6(b)) were formed when PVP (30 g) having molecular weight of 10,000 was used, while the size distribution of the formed silica particles (Figures 6(c) and 6(d)) was broadened when PVPs (30 g) having higher molecular weight than 55,000 were used. The similar results were observed with the reaction mixture containing ethanol as solvent. These results indicate that the addition of PVP and the increase of its molecular weight broaden the size distribution of the formed silica particles even though reduction in the particles size was observed. Because of this, PVP ($\overline{M}_w$ = 10,000) was used in the following experiments.

Silica nanoparticles whose size is below 20 nm can be prepared by controlling the composition of reactant, solvent, reaction temperature, or by adding PVP. Comparing the results obtained in the previous research[26] with those obtained here, control of reaction temperature or addition of PVP is more effective way in retarding aggregates formation than composition control of reaction mixture, even though the aggregates were still formed when the primary silica particles were smaller than 20 nm. Based on this, various amounts of PVP ($\overline{M}_w$ = 10,000) were added to the reaction mixtures and then they were reacted at a fixed temperature of 60 °C to fabricate silica nanoparticles without the aggregates formation. The particles size was gradually decreased from 30 to 3 nm by increasing PVP content in reaction mixture as shown in Figure 7. The aggregates were not formed even though the size of formed primary particles was smaller than 20 nm (see Figure 8). Since PVP is soluble in water, the silica nanoparticles can be easily obtained by washing
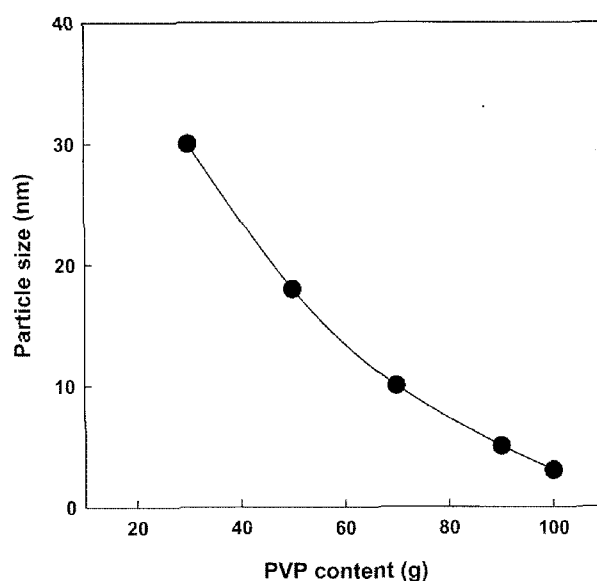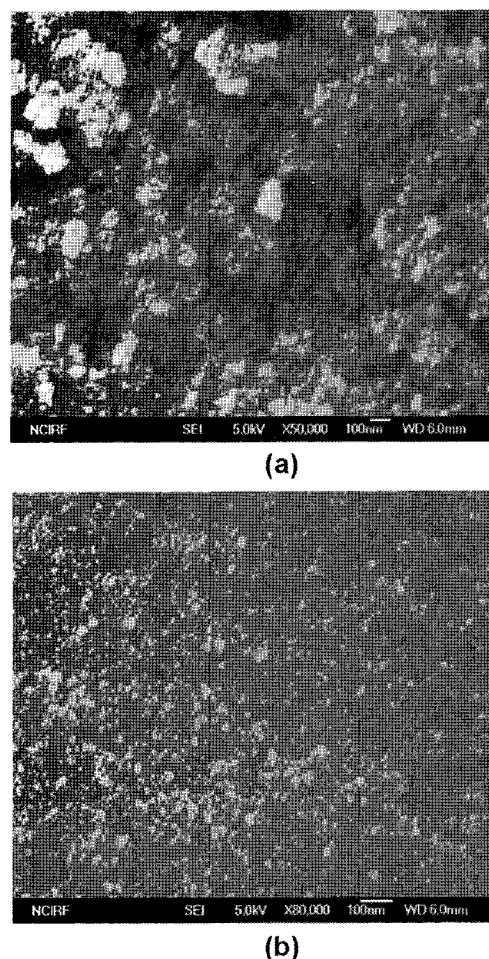

Figure 7. Effects of PVP ($\overline{M}_w$ = 1,000) content in the reaction mixture on the size of the silica nanoparticles when reaction temperature was fixed to 60 °C.
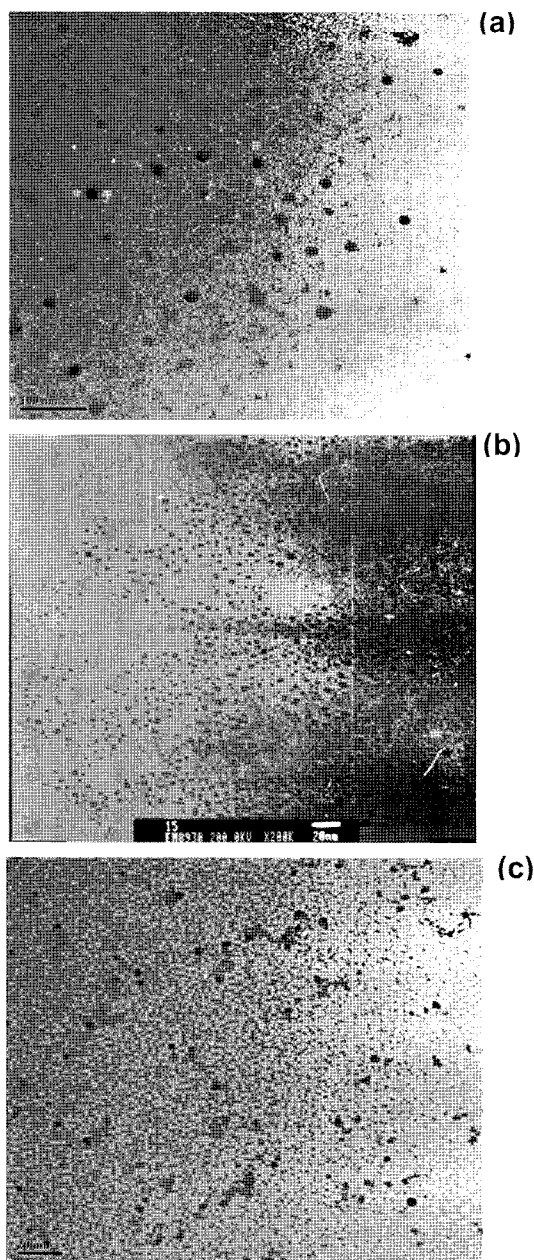
Figure 8. TEM microphotographs of the silica nanoparticles synthesized by changing amounts of PVP ($\overline{M}_w$ = 10,000) were added to the reaction mixtures; (a) PVP (50 g, 18 nm), (b) PVP (90 g, 5 nm), and (c) PVP (100 g, 3 nm).

Figure 9. FE-SEM microphotographs exhibiting cross sectional morphologies of dental composites containing 10 wt% of silica nanoparticles; (a) without surface treatment and (b) with surface treatment.

with deionized water after centrifuge. As summary, nearly monodispersed silica nanoparticles without formation of the aggregates could be synthesized by controlling reaction temperature and by adding PVP ($\overline{M}_w$ = 10,000) to the reaction mixture.

Composite Preparation with Silica Nanoparticles. To explore the effects of surface treatment with the γ-MPS on the particles dispersion in the resin matrix, composites containing surface treated silica nanoparticles (18 nm) or

untreated silica nanoparticles were prepared. The resin matrix used here consists of 70 wt% of Bis-GMA as a base resin and 30 wt% of TEGDMA as a diluent. Figure 9 exhibited cross sectional morphologies of dental composites containing 10 wt% of surface treated (or untreated) silica nanoparticles observed with FE-SEM. Dispersion of treated particles in the resin matrix was much better than that of untreated particles. Composites prepared from the untreated particles contained particles aggregates, while those prepared from the treated particles did not contain particles aggregates. Enhanced dispersion in the resin matrix of the treated silica particles might come from the chemical bonding between methacrylate groups in γ-MPS and that in the resin matrix as well as hydrophobic interactions between resin matrix and grafted γ-MPS. As summary, nanocomposites containing finely dispersed silica nanoparticles could be fabricated by using surface treated silica nanoparticles prepared here.

Summary

Nearly monodispersed silica nanoparticles smaller than 25 nm were synthesized via a modified Stöber method. To control particles size and prevent the aggregates formation, kind of solvent, reaction temperature, and reaction medium were changed. The particles size was reduced in the order of isopropanol, ethanol, and methanol when compositions of reaction mixtures and reaction conditions were fixed. The particles size was also reduced by increasing reaction temperature and PVP content in the reaction mixture. Even though silica nanoparticles synthesized by Stöber method form aggregates when size of silica nanoparticles is smaller than 25 nm, formation of aggregates with primary silica nanoparticles smaller than 25 nm could be prevented by increasing reaction temperature and amount of PVP added to the reaction mixture. Dental nanocompsites containing finely dispersed silica nanoparticles in an organic matrix could be fabricated by using the surface treated silica nanoparticles with the γ-MPS. The effects of the nanofiller inclusion in the dental composites on the wear and fatigue resistance will be the topic of a forthcoming paper.

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