Fabrication and Properties of Surface-Modified β-Si$_3$N$_4$ Whiskers Reinforced Dental Resin Composites

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ABSTRACT: In this article, three kinds of surface-modified methods were used to treat β-Si$_3$N$_4$ whiskers before being incorporated into Bis-GMA/TEGDMA dental resin matrix in order to improve the whiskers' reinforcing effect. The experimental results showed that composites with directly heat-treated and then silanized β-Si$_3$N$_4$ whiskers had the best reinforcing effect. They had flexural strength of 160 ± 7.0 MPa (mean ± SD; $n = 6$), compressive strength of 371 ± 1.4 MPa (mean ± SD; $n = 5$) and HRA of 48.4 ± 0.5(mean ± SD; $n = 5$), respectively. In addition, water sorption and solubility test demonstrated that the composites were reliable to use as the dental restoration materials. Therefore, the directly heat-treated and then silanized β-Si$_3$N$_4$ whiskers (better than β-Si$_3$N$_4$ whiskers mixed with SiO$_2$ nanoparticles or SiO$_2$ sols) were most suitable fillers to reinforce dental resin composites. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Dental resin composites were composed of polymerizable organic resin matrix and inorganic fillers.[1,2] The composites showed many advantages such as good mechanical properties, excellent esthetic quality and the outstanding ability to bond to enamel surface.[3] Inorganic fillers, organic resin matrix and the silane coupling agents were three key factors influencing the mechanical properties of dental resin composites.[1,4,5]

At present, the fillers in commercial available composites mainly included quartz, gaseous SiO$_2$, zirconia,[6] hydroxyapatite,[7] SiO$_2$ glass,[2,8] and so on. These fillers all had the potential to improve the mechanical properties and modulus of elasticity. In the mean time, the fillers could also reduce polymerization shrinkage, water absorption and thermal expansion of dental composites.[1] However, the flexural strength of these dental composites mainly ranged from 100 to 140 MPa, which inhibited their applications in large bulk restorations.

More recently, dental composites reinforced with high-strength fibers/whiskers had resulted in dramatic improvements on mechanical properties.[9–11] Xu and coworkers revealed that the impregnation of extremely strong ceramic fibers/whiskers such as silicon nitride and silicon carbide could lead to a twofold increase in strength and toughness. Meanwhile, the polishability,

water absorption and strength durability were also enhanced. Silicon nitride (Si$_3$N$_4$) ceramics exhibited outstanding mechanical properties and thermo-mechanical properties,[12,13] which made Si$_3$N$_4$ ceramics have many applications such as cutting tools, ball bearings, sealing elements and engine components. β-Si$_3$N$_4$ whiskers, which had many excellent mechanical properties including fracture toughness, hardness, friction and wear coefficients, were used as the reinforce phase to modify the mechanical properties of composites to meet the requirements for many high-load medical applications in human body.

In this article, β-Si$_3$N$_4$ whiskers were used to reinforce Bis-GMA/TEGDMA dental resin and three different dental restoration composites were fabricated. Their mechanical properties (including flexural strength, elastic modulus, compressive strength, and HRA) were investigated. Moreover, the influences of surface-modified methods for β-Si$_3$N$_4$ whiskers on the reinforcing effects of their samples were also discussed.

MATERIALS AND METHODS

Synthesis and Surface Treatment of β-Si$_3$N$_4$ Whiskers

β-Si$_3$N$_4$ whiskers applied in this study were synthesized in our laboratory, they were single-crystalline silicon nitride (β-Si$_3$N$_4$) with diameters ranging from 0.1 to 1 μm (mean = 0.4 μm) and length ranged from 0.9 to 10 μm (mean = 3 μm). Before being

incorporated into dental resin matrix, β-Si$_3$N$_4$ whiskers were further surface-modified by one of the following three ways.

Method A. β-Si$_3$N$_4$ whiskers were mixed with SiO$_2$ nanoparticles (200 nm) with mass ratio of 2:1 (β-Si$_3$N$_4$ whisker: SiO$_2$). Their mixtures were then mechanically milled for 12–24 h.

Method B. β-Si$_3$N$_4$ whiskers were dispersed into a SiO$_2$ sol with mass ratio of 2:1(β-Si$_3$N$_4$ whisker: SiO$_2$) and followed by vigorously mechanical stirring until the mixture became a uniform solid. The mixture was then dried in a furnace at 60°C for 12 h.

Method C. β-Si$_3$N$_4$ whiskers were directly used without any additive. Finally, all the three kinds of pre-treated β-Si$_3$N$_4$ whiskers were further heated in a furnace under air atmosphere at 900°C for 2 h and then were silanized in cyclohexane with γ-Methacryloxypropyl trimethoxy silane (mass fraction of 5 wt % to whiskers) and n-propylamine (mass fraction of 3 wt % to whiskers) in a 90°C water bath until they completely dry. The whiskers treated by Method A, B, and C were defined as A, B, and C modified whiskers, respectively.

Specimen Fabrication

At first, dental resin matrix, which consisted of mass fractions of 48.975 wt % Bis-GMA (bisphenol glycidyl dimethacrylate), 48.975 wt % TEGDMA (triethylene glycol dimethacrylate), 0.05 wt % 2,6-di-tert-butyl-4-methylphenol (BHT), and 2 wt % benzoyl peroxide, was fabricated. Then, the A, B, and C modified whiskers were magnetically stirred with the dental resin matrix at fixed mass ratio of 50 wt % to form pastes. After the pastes were poured into molds and heat-cured in an oven at 140°C for 30 min, their composites were obtained. In addition, the specimens of pure dental resin were also fabricated using the similar procedures.

Characterization of β-Si$_3$N$_4$ Whisker and Its Reinforced Dental Resin Composites

The morphology of β-Si$_3$N$_4$ whiskers and microstructure of the composites were observed by scanning electron microscopy (SEM) (Model JXA-8100, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) (JEM-2100F, Tokyo, Japan). Specimens were machined into a rectangle bar with dimension of $2 \times 2 \times 25$ mm^3 to measure the flexural strength and elastic modulus via three point bending test (Model AUTOGRAPH AG-I, Shimadzu, Japan), the support distance of 20 mm and a cross-head speed of 1 mm/min were used. Specimens were machined into a cylinder of Φ 4.5 $\times$ 8 mm^2 to measure compressive strength. Each specimen was loaded in compression until failure using an Instron 5592 mechanical testing machine (Instron 5592, Pennsylvania, USA) with a crosshead speed of 1 mm/min. For hardness testing, specimens were machined into a cylinder of Φ10 $\times$ 6 mm^2. Each specimen was tested by the machine of Instron Wilson Rockwell Series 2000 (Pennsylvania, USA) using HRA with 60 kg load.

For water sorption and solubility testing,[14] specimens were machined into a cylinder of Φ15 $\times$ 1 mm^2. Five discs were prepared for each composite. The discs were placed in a desiccator and weighed until a constant mass (m_1) was obtained. The discs were immersed in distilled water at 37°C for 7 days, then using dried cloth to remove the water absorbed on the surfaces of samples and weighed (m_2). A constant mass (m_3) was further obtained by subsequently drying the specimens at 110°C in an oven. The diameter and the thickness of the specimen were measured at five points and the volume (V) was calculated in cubic millimeters. The values of water sorption (W_{sp}) and solubility (W_{sl}) were calculated for each disc using the following formulae:

$$W_{sp} = \frac{m2 - m3}{V} \qquad W_{sl} = \frac{m1 - m3}{V}$$

Means and standard deviations (S.D.) of the reported data for all the experimental groups, were calculated. The results were statistically analyzed by one-way analysis of variance. The *post hoc* multiple comparisons were performed by Tukey's test. A P value less than 0.05 was considered statistically significant.

RESULTS AND DISCUSSION

The SEM/TEM images in Figure 1 showed the representative morphologies of β-Si$_3$N$_4$ whiskers modified by Method A (a,b), B (c,d), and C (e,f). Figure 1(a) showed SiO$_2$ particles were thermally fused onto the surface of β-Si$_3$N$_4$ whiskers. The arrow on the left showed an area of whiskers surface relatively densely coated with SiO$_2$ particles and the arrow on the right indicated an area of whiskers surface less densely coated with SiO$_2$ particles, as shown in Figure 1(b). All the surface of the whiskers were equally enwrapped by SiO$_2$ in Figure 1(d). However, SiO$_2$ particles tended to bond the whiskers together as aggregates, as shown in Figure 1(c). Figure 1(e) indicated a uniform thin layer of SiO$_2$ could be detected on the surface of whiskers, the thickness of SiO$_2$ layer was about 7–10 nm due to Si$_3$N$_4$ whiskers oxidation during heat-treatment [Figure 1(f)].

Low and high resolution SEM images in Figure 2 showed the representative fracture surface of the composites with A modified whiskers (a, b), the composites with B modified whiskers (c, d) and the composites with C modified whiskers (e, f). A whiskers were uniformly dispersed in dental resin matrix [Figure 2(a)]. It was clearly that whiskers were pulled out of the dental resin matrix and the surfaces of whiskers were rather smooth [Figure 2(b)]. The reason was that SiO$_2$ was only discretely coated on the surface of A whiskers. In contrast to method A, whisker clusters were observed in the composites with whiskers modified by method B [Figure 2(c)]. Moreover, the whiskers were bonded into clusters by SiO$_2$. Due to the aggregations of these whisker clusters, they would definitely weaken the reinforcement effect of B modified whiskers. However, the surfaces of whiskers in Figure 2(d), which had been pulled out from dental matrix, were rather coarse and covered by some dental resin remnants. The result indicated that an excellent adhesion existed between the whiskers and dental resin matrix. The distribution of whiskers was uniform as shown in Figure 2(e), and typical bonding interface were observed (as indicated by the arrow in Figure 2(f)), implying their microscopic dispersibility and adhesion between whiskers and dental resin were better than the other two methods. The reason was that SiO$_2$ thin film *in situ* originated from C modified Si$_3$N$_4$ whiskers, resulting in a uniform distribution and strong adhesion in dental resin matrix, both of the factors will benefit for the mechanical properties of the composites. So, the different surface-modify methods of whiskers dramatically affected the distribution and adhesion of whiskers in dental resin matrix, which would inevitably influence their mechanical properties.

Figure 3 exhibited that the flexural strength of A, B, and C modified whiskers reinforced dental resin composites. The flexural strength of A, B, and C modified whiskers reinforced dental
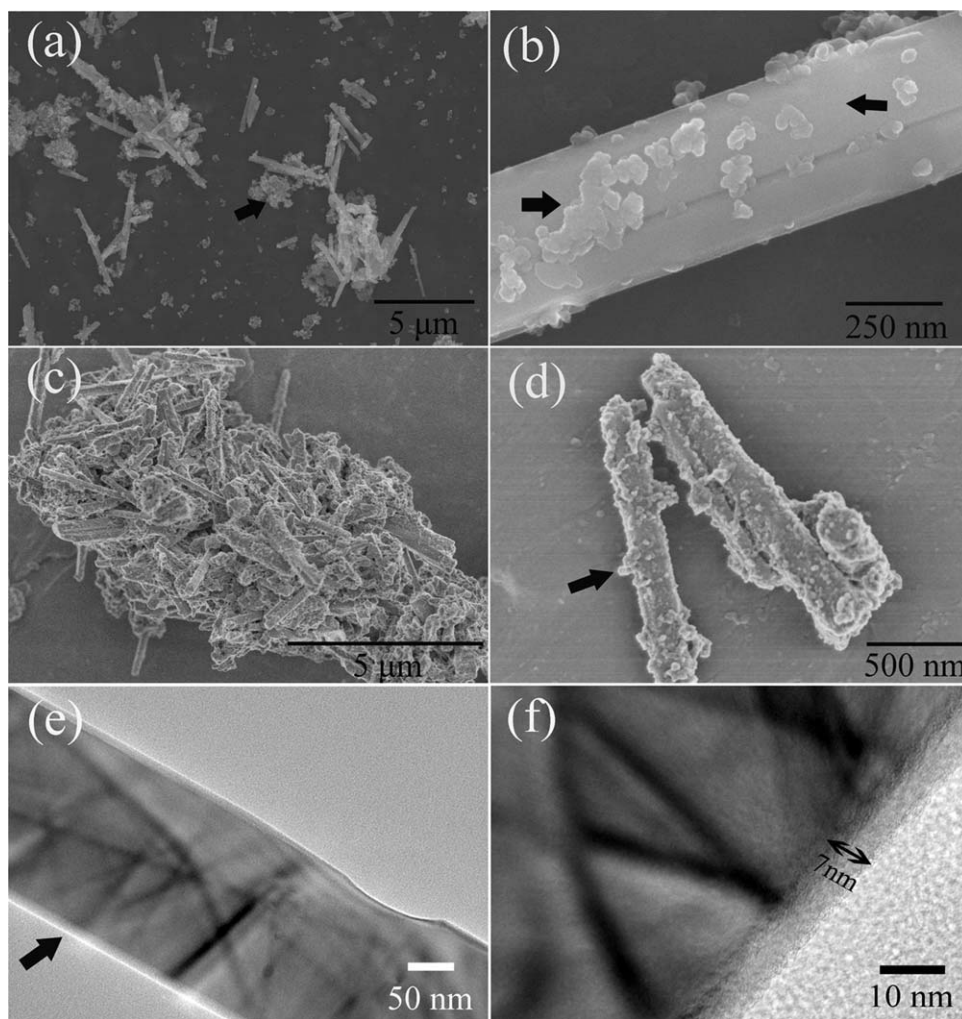
Figure 1. SEM/TEM images of β-Si$_3$N$_4$ whiskers after surface-modification (a,b) by method A, (c,d) by method B and (e,f) by method C.

resin composites were 134.7 ± 6.3 MPa (mean $\pm$ SD; n=6), 112 ± 6.2 MPa and 160 ± 7 MPa, respectively. The flexural strength of Si$_3$N$_4$ whiskers reinforced composites was much higher than that of pure dental resin, which was 79.85 ± 0.2 MPa. It could be found that the flexural strength of A modified whiskers reinforced composites was higher than that of B. The main reason was that whisker clusters appearing in method B were harmful for the uniform distribution of whiskers and densification of the composites, and became the weak points during fracture process. The C modified whiskers reinforced composites displayed the highest flexural strength due to three possible reasons, (1)whiskers were uniformly dispersed in the dental resin composites, (2) the thin SiO$_2$ layer on the surface of whiskers, which could effectively function as bridge between the whiskers and dental resin matrix and ensure excellent adhesion of whiskers in their reinforced composites, (3) the mass ratio of whiskers to SiO$_2$ might be higher than 2:1, since only a thin layer of (7–10 nm) SiO$_2$ was produced on the surface of C modified whiskers and resulted in higher proportion of whiskers than other two methods. Therefore, C modified method was most appropriate to enhance the flexural strength.

The compressive strength displayed in Figure 4 increased from 103.5 ± 4.9 MPa (mean $\pm$ SD; $n = 5$) for the pure dental resin to a much higher value of 379.5 ± 27.6 MPa for composites with A modified whisker. Meanwhile, the compressive strength of composites with B and C modified whisker were slightly lower, and they were 272.7 ± 15 MPa and 371 ± 1.4 MPa, respectively. Consequently, the dental composites originating from A modified whiskers were considered to be the best in compressive properties. The concrete reasons should be that SiO$_2$ nanoparticles in A modified whiskers also contributed to the compressive strength because SiO$_2$ nanoparticles may just filled the gap left by rod-like β-Si$_3$N$_4$ whiskers, and whiskers agglomerates/clusters in composites with B modified whiskers could weaken the whiskers' reinforcement effect.

The hardness of the three composites was more than two times higher than that of pure dental resin, but it had very small changes among the three composites (Figure 5). The hardness values for the composites with A, B, and C modified whiskers were about 50.5 ± 0.3, 47.5 ± 2.8 and 48.4 ± 0.5 (mean $\pm$ SD; $n = 5$), respectively. So, the incorporations of β-Si$_3$N$_4$ whiskers into dental resin matrices could obviously enhance
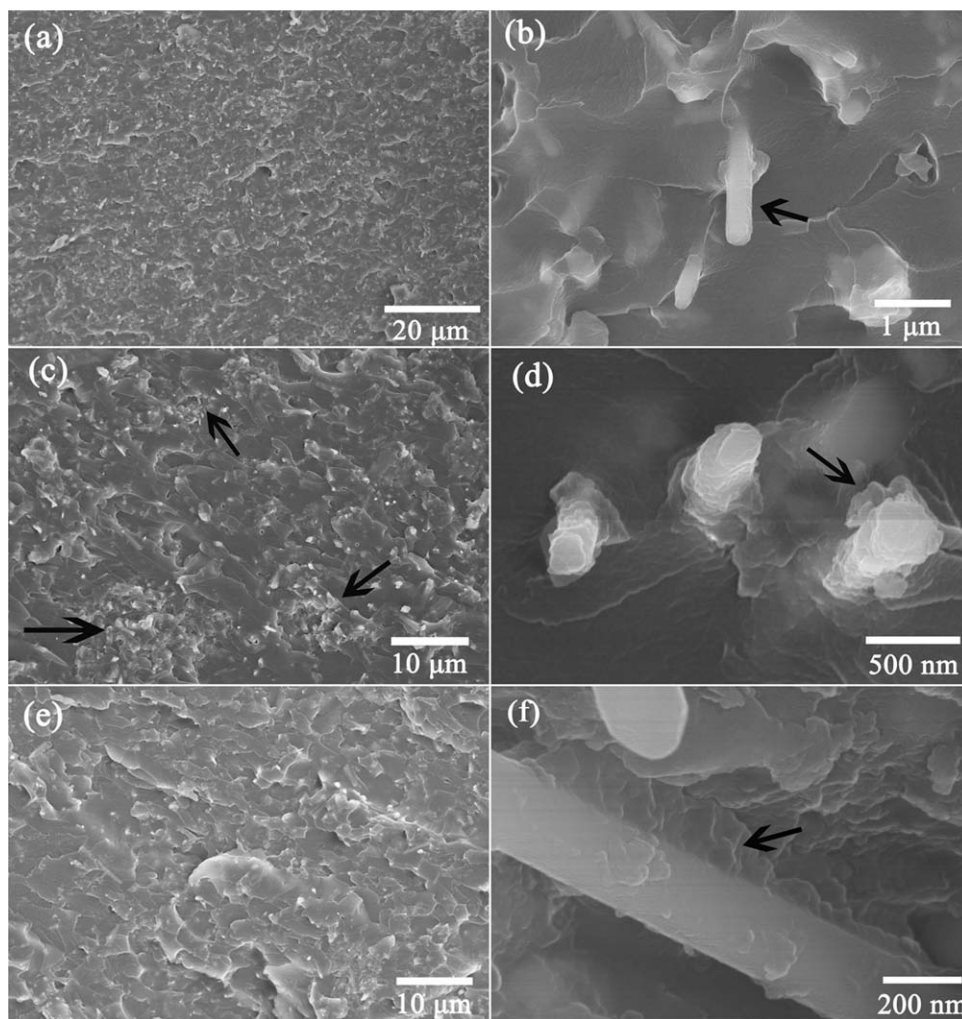
Figure 2. SEM images of fracture surface of β-Si$_3$N$_4$ whiskers reinforced dental resin composites at filler ratio of 50 wt % (a) with A modified whisker, with an amplified image in (b); (c) with B modified whisker, with an amplified image in(d); (e)with C modified whisker, with an amplified image in(f).

their hardness, which could be attributed to the higher hardness of β-Si$_3$N$_4$ whiskers.

The mechanical properties of whiskers reinforced dental composites were almost two times than that of pure dental resin.[13,15]

The reinforcing mechanism included five aspects. (1) The rod-like β-Si$_3$N$_4$ whiskers contributed to the flexural strength of composites by requirement of more energy to overcome the interfacial resistance during β-Si$_3$N$_4$ whiskers pull-out process.
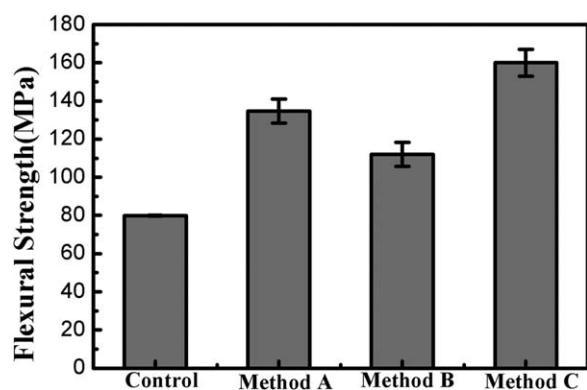

Figure 3. Flexural strength of A, B, and C modified whiskers reinforced Bis-GMA/TEGDMA dental resin composites.
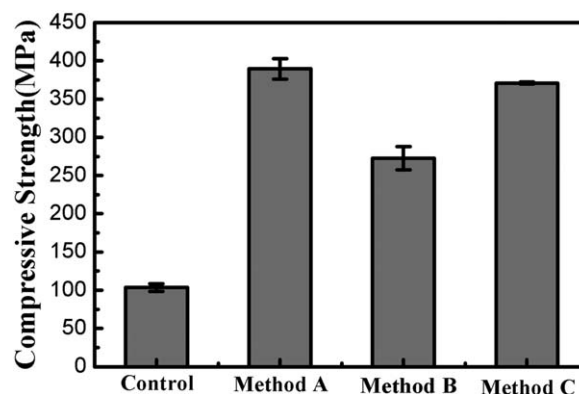

Figure 4. Compressive strength of A, B, and C modified whiskers reinforced Bis-GMA/TEGDMA dental resin composites.
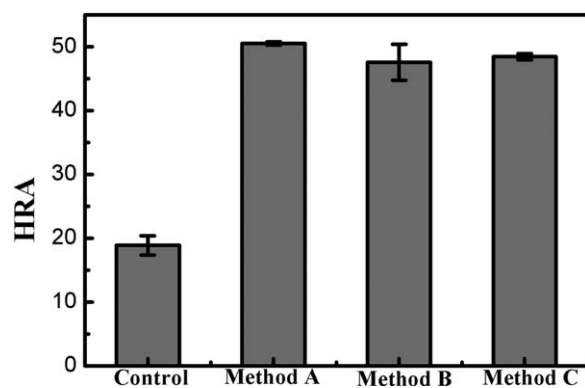
Figure 5. HRA of A, B, and C modified whiskers reinforced Bis-GMA/TEGDMA dental resin composites.

(2) Under the effect of the stress field, the interfacial bonding stress that was close to the crack tip, resulting in the interfacial debonding phenomenon of the rod-like β-Si_3N_4 whiskers. The crack bridging of the rod-like β-Si_3N_4 whiskers reduced the stress concentration of crack tip, increased the crack progress resistance. (3) The primary strength of dental resin also contributed to the mechanical properties of the composites. (4) The intergranular fracture of the β-Si_3N_4 whiskers contributed to mechanical properties of composites by crack deflection. (5) The strong covalent bond between inorganic fillers and the organic matrix was essential for obtaining good mechanical properties in dental composites. Bonding of two phases was achieved by coating the fillers with a silane coupling agent[16] that had functional groups to link the fillers and the matrix. In this experiment, the silane used was 3-methacryloxypropyltri-methoxysilane, one end of the coupling agent could be bonded to the hydroxyl groups of SiO_2 particles, and the other end was capable of copolymerizing into the Bis-GMA/TEGDMA dental resin matrix.[1] Through the bonding between SiO_2 particles and dental resin matrix, the whiskers were tightly linked to the dental resin matrix. So, we could expect whiskers' excellent retention in the dental resin matrix. The dental remnants on the whiskers surfaces [Figure 2(b,d,f)] after being pulled-out demonstrated that effective adhesion were formed between the whiskers and dental resin matrix. During fracture process, the pulled-out whiskers with remnant on the surface further consumed energy by forming steps and additional fracture surface area.

Water sorption and water solubility values were presented in Table I. The water sorption for each composite was not greatly different. However, the water solubility of the composites with C modified whiskers was lowest. According to ISO 4049:2000 standard for dental restorative composites, water sorption and solubility of dental material must be lower than 40 mg/mm^3 and 7.5 mg/mm^3, respectively. The values of water sorption for the composites with A, B, and C modified whiskers, were all within the range of the ISO's standard. However, the water solubility of the composites with A modified whiskers were higher than the ISO's standard. The higher values of water solubility in our experiments might be caused by the releasing of SiO_2 nanopowders from the dental matrix. Since SiO_2 nanoparticles were easy to release form the matrix and dissolve in water, resulting in the reductions of mass for composites. As a result, the higher values of water solubility appeared in the composites with A modified β-Si_3N_4 whiskers. These speculations were directly supported by their SEM pictures. As shown in Figure 1(a), only small fraction of SiO_2 nanopowders were fused onto the surface of β-Si_3N_4 whiskers while most of SiO_2 nanopowders either formed SiO_2 agglomerates or dispersed discretely in dental resin matrix.

CONCLUSIONS

Surface-modified β-Si_3N_4 could greatly improve the mechanical properties of dental resin composites. The flexural strength of composites reinforced with A and C modified whiskers almost improved two times compared with the control group. Since β-Si_3N_4 whiskers agglomerates/clusters would weaken the densification of the composite, the composites with B modified whiskers did not appear excellent mechanical reinforcement effects. The composites with C modified whiskers had highest flexural strength of 160 MPa and suitable water sorption and solubility. Therefore, C modified whiskers were considered to be a good filler candidate to reinforce the dental resin composites.

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Table I. Values of Water Sorption, Solubility of Composites with A, B, and C Modified Whiskers

Group	W_{sp} (µg/mm^3)	W_{sl} (µg/mm^3)
With A whiskers	19.65 ± 7.02	11.87 ± 0.03
With B whiskers	29.6 ± 6.34	5.47 ± 4.23
With C whiskers	25.9 ± 5.03	2.04 ± 3.7

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