

The Mechanical Properties of β -Si₃N₄ Whiskers-Reinforced Dental Resin Composites

Kai-Hui Zuo,¹ Li-Min Lu,² Yu-Ping Zeng¹

¹State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai 200050, China

²Systems Design Engineering, University of Waterloo, City of Waterloo, Canada

Correspondence to: Y.-P. Zeng (E-mail: yuping-zeng@mail.sic.ac.cn)

ABSTRACT: The surface-modified β -Si₃N₄ whiskers were used as inorganic fillers to reinforce dental resin (Bis-GMA/TEGDMA) matrix with filler level ranging from 0 to 60 wt %. The experimental results indicated that the fracture strength of the composites increased from 79.85 to 139.8 MPa with increasing the whiskers loading. The compressive strength, elastic modulus, and rockwell hardness all increased monotonously with increasing filler level. Furthermore, thermal cycling did not decrease the fracture strength of the composites. Moreover, the composites showed good biocompatibility to support MG63 cells adhesion and proliferation. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40692.

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INTRODUCTION

Dental composites typically consist of a resin matrix and glass or ceramic fillers as reinforcements.^{1,2} However, mostly composites are inadequate as bulk restoratives. It is known that suitable fillers have the potential to improve the mechanical properties and modulus of elasticity. Recently, the silicon nitride (Si₃N₄) whiskers have been used as the fillers because they can result in high bending strength and toughness of composites.^{3,4} For example, the tensile strength of β -Si₃N₄ whiskers is ~50 GPa, compared to ~3GPa for glass fibers and 0.1 GPa for bulk glass.⁵ The fracture toughness of silicon nitride is nearly 10–12 MPa.m^{1/2},³ whereas that of glass is about 0.7 MPa.m^{1/2}.⁶ In addition, the elongated β -Si₃N₄ whiskers (e.g., a diameter of 0.3 μ m and a length of 3 μ m) used to reinforce dental resin composites have the potential of bridging micro-cracks and resisting them from propagating, as well as preventing dislodgment from the composites during wear process.^{5–8} However, the mechanical properties of dental composites with β -Si₃N₄ whiskers cannot fully meet the requirements and little attention has been paid to the thermal cycling effect and biocompatibility of the composites.^{9,10}

To improve the binding force between the filler and resin and the mechanical properties of dental composites, before mixing the filler with the resin matrix, the surface coupling agent is commonly used. However, the coupling agent cannot fully wrap the filler surface, and thus the enhanced action is not sufficient.

Therefore, before using the coupling agent, surface modification of the filler may effectively improve the mechanical properties.¹¹

Herein, the composites reinforced with surface-modified β -Si₃N₄ whisker at different filler levels were fabricated. The mechanical properties were tested before and after thermal cycling. In addition, the adhesion and proliferation of MG63 cells on the composites was investigated to evaluate the biocompatibility of the composites.

MATERIALS AND METHODS

Preparation of β -Si₃N₄ Whiskers

The β -Si₃N₄ whiskers as filler agent were synthesized in our laboratory. The diameters ranged from 0.1 to 1 μ m (mean = 0.4 μ m) and lengths ranged from 0.9 to 10 μ m (mean = 3 μ m). Before mixing the β -Si₃N₄ fillers with the resin, the β -Si₃N₄ were directly heated in a furnace in air at 900°C for 2 h to form SiO₂ layers on the surfaces. Then, the whiskers 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 dry.

Fabrication of β -Si₃N₄/Bis-GMA Composites

The dental resin matrix consisted 48.975 wt % Bis-GMA (bisphenol glycidyl dimethacrylate), 48.97 wt % TEGDMA (triethylene glycol dimethacrylate), 0.05 wt % 2,6-di-tert-butyl-4-methylphenol (BHT), and 2 wt % benzoyl peroxide (BPO). The fabrication of β -Si₃N₄/Bis-GMA composites was as followings.

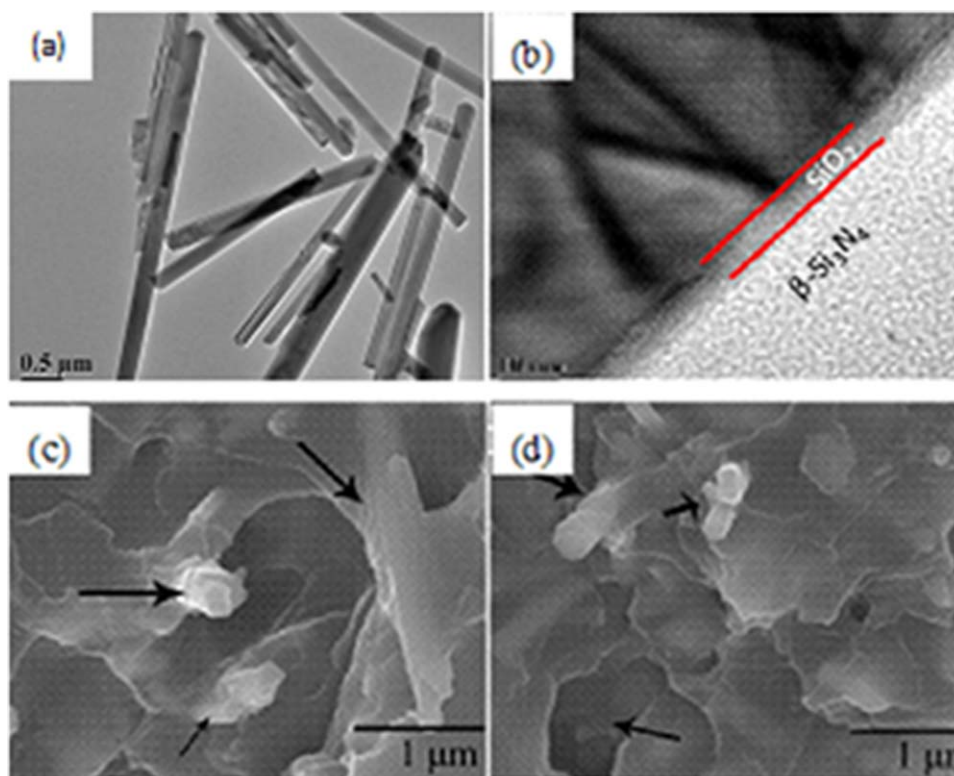


Figure 1. TEM micrographs of β - Si_3N_4 whiskers and SEM micrographs of fracture surfaces of whiskers-reinforced dental resin matrix composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

First, the surface-modified β - Si_3N_4 whiskers were dispersed into dental resin matrix with levels ranging from 0 to 60 wt %. Then, the mixed substances were degassed in a vacuum oven for 5 min to remove air bubbles before being poured into molds. Last, the mixed substances were thermal solidified at 140°C for 30 min to get dental composites.

Characters of β - Si_3N_4 /Bis-GMA Composites

The morphologies of samples with gold coating were observed by scanning electron microscopy (SEM, Model JXA-8100, JEOL, Tokyo, Japan), and the morphology of β - Si_3N_4 whiskers was observed by transmission electron microscope (TEM, HRTEM, JEM-200CX, Japan) with an accelerating voltage of 80 kV. Five specimens were machined to a dimension of $2 \times 2 \times 25 \text{ mm}^3$ to test the fracture strength and elastic modulus via the three-point bending test (Instron 5500R universal testing machine, Instron Ltd., USA.) with a support distance of 20.0 mm and a cross-head speed of 1 mm/min. The compress strength was measured using five cylinder samples of $\Phi 4.5 \times 8 \text{ mm}^2$ (Instron 4411, USA) with a cross-head speed of 1 mm/min. The Rockwell hardness (HRA) was measured by the machine of Instron Wilson Rockwell Series 2000 using HRA with 60 Kg load using cylinders of $\Phi 10 \times 6 \text{ mm}^2$. There were five samples without β - Si_3N_4 whisker and five samples containing 50 wt % β - Si_3N_4 whiskers used to do the thermal cycling test. These samples were firstly immersed in water of 37°C for 30 days. Then, the specimens were subjected to 500 thermal cycles in water baths of 5 and 55°C with a 30 s immersion at each temperature. After drying, the fracture strength of these samples was measured.

The biocompatibility was measured by the following method. The material disks ($\Phi 10 \times 2 \text{ mm}^2$) were sterilized by autoclave. MG63 cells were seeded onto the disks at a density of $5 \times 10^3 \text{ cm}^2$ in a 24-well tissue culture plate and incubated in Dulbecco's modified Eagle's medium (DMEM, Gibco, USA) with 10% (v/v) fetal calf serum plus antibiotics maintained at 37°C in a humidified atmosphere of 95% air and 5% CO_2 . The tissue culture plates were used as blank control. The cells were cultured for 1, 3, and 6 days. The medium was refreshed at day 3. At each time point, cell proliferation was tested by 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT, Sigma, USA) colorimetric method. In brief, 100 μL of 5 mg/mL MTT solution was added. After additional incubation for 4 h, the DMEM-MTT solution was removed and replaced with 400 μL of di-methyl sulfoxide. A total of 100 μL of the reacted reagent from each well was transferred to a 96-well plate, and the optical density was read at 490 nm using an enzyme-linked immunosorbent assay plate reader (ELx 800, BIO-Tek, USA). For SEM observation, the disks after fixation in 2.5% glutaraldehyde were dehydrated in a gradient ethanol solution ((v/v), 30%, 50%, 70%, 90%, 95%, and 100%) for 10 min and finally air dried in hexamethyl disilazane. The specimens were then sputter-coated with gold and viewed by SEM.

RESULTS AND DISCUSSION

The TEM micrographs of β - Si_3N_4 whiskers and SEM micrographs of dental composites containing β - Si_3N_4 whiskers are shown in Figure 1. Comparing Figure 1(a) with Figure 1(b), there

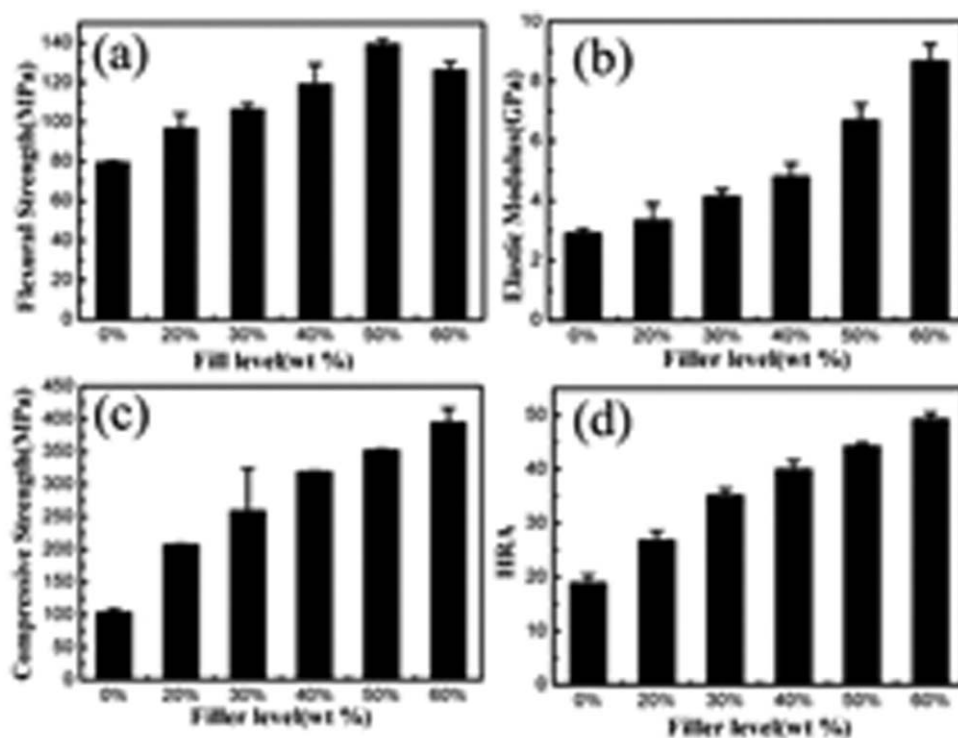


Figure 2. Mechanical properties of the resin composites containing β -Si₃N₄ whiskers.

is a SiO₂ layer uniformly distributed on the surface of β -Si₃N₄ whisker. It is reported that the silanized β -Si₃N₄ whiskers with SiO₂ layers have better adhesion with the dental resin.¹¹ Figure 1(a) also indicates that β -Si₃N₄ whiskers are scattered and there is no neck-connection, which also helps to disperse in the organic matrix. Figure 1(c) indicates that β -Si₃N₄ whiskers are uniformly distributed in the matrix at the filler level of 50 wt %. However, discrete distribution is observed at higher filler level of 60 wt %, which is not conducive to densification. Figure 1(c,d) also shows that there are residual resins on the surface of β -Si₃N₄ whiskers pulled out from the resin matrix. The reason is the β -Si₃N₄ whiskers encounter large resistance from the resin matrix, which indicates that the binding force between β -Si₃N₄ whiskers and the resin matrix are very good.

The mechanical properties of β -Si₃N₄ whiskers-reinforced resin composites are shown in Figure 2. Results indicate that the mechanical properties of composites, including the flexural strength, elastic modulus, compressive stress, and HRA, are significantly higher than those of pure dental resin. The elastic modulus, compressive strength, and HRA all increase with increasing the content of fill. However, the flexural strength reaches the highest point of 139.8 MPa at the filler ratio of 50 wt % and decreased to 126.7 MPa as the filler ratio further increases to 60 wt %. It is known that the β -Si₃N₄ whiskers can make cracks pinning and deflection, and the pulling out of β -Si₃N₄ whiskers from the matrix consumes lots of energy. At the same time, β -Si₃N₄ whiskers have higher fracture strength and elastic modulus than those of matrix. These both contribute to the excellent mechanical properties of composites. However, 60 wt % β -Si₃N₄ whiskers are difficult to be uniformly dispersed

in matrix. This results in a low densification of composites, which decreases the flexural strength. For the values of mechanical tests are close in some conditions, a T test was used to analyze whether the strength change significantly. Comparing the flexural strength of composites with 40% and 50%, the value of *t* is 7, which was higher than 2.776 from the table of T values. The result showed that the strength significantly changed.

Figure 3 shows the flexural strength of resin and resin composites containing 50 wt % β -Si₃N₄ whiskers, which are dealt with and without thermal cycling test. Results indicate that the hydrothermal cycling almost do not decrease the flexural strength of the resin composites containing 50 wt % β -Si₃N₄. However, the hydrothermal cycling obviously decreases the flexural strength of resins without whiskers. The reason is that the good binding between the whiskers and resins effectively

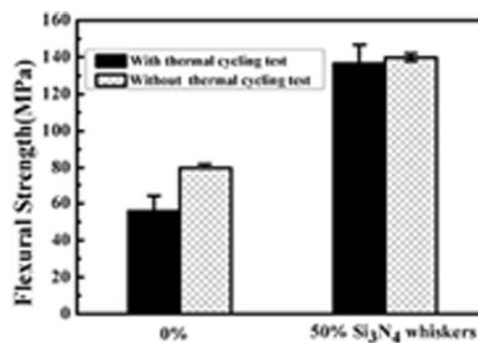


Figure 3. Flexural strength of composites dealt with and without thermal cycling test.

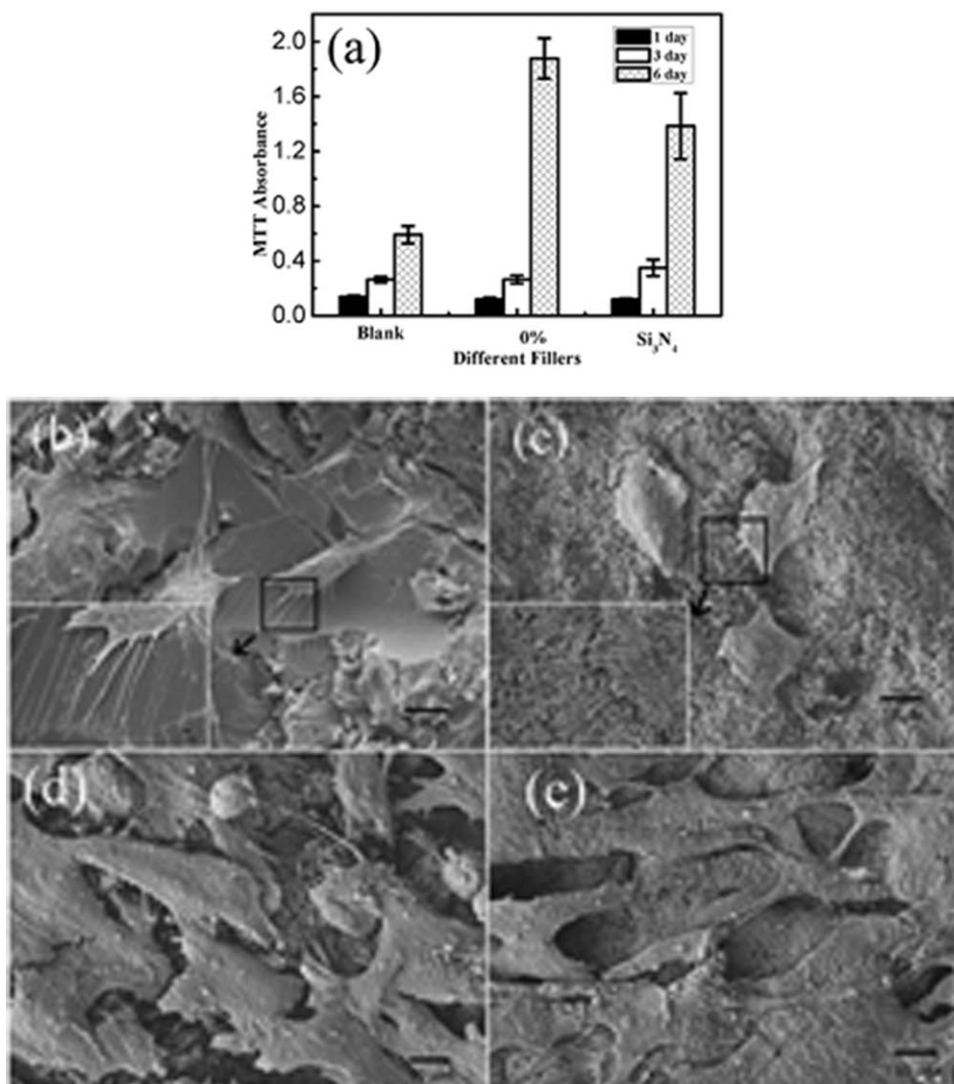


Figure 4. The MTT absorbance values and morphologies of cells proliferations.

prevents the expansion of cracks. The results also show that the standard deviations for the composites through thermal cycling test are higher than those of composites without thermal cycling test. The standard deviation is the discrete degree between individuals. Therefore, the stability of the material is not good. Because the dental material need stable performance in an alternating hot and cold environment, the further improved and in-depth research in the stability is need.

The MTT absorbance values and morphologies of cells proliferations on the resin and resin composites are presented in Figure 4. Comparing with the black group, the absorbance value of the experimental group obtained after culturing 1 day is less, but the value after 6 days is higher. The results indicate that pure resin and resin composite containing 50 wt % β -Si₃N₄ filler contribute to cell growth. The Figure 4(b,c) show the cell can spread out on the surface of resin after culturing 1 day. However there are many tentacles stretching out, which indicate that the cell growth is not very good. After cells growing 6 days, the cells almost cover the surface of resin and resin composites [shown in Figure 4(d,e)],

which reveal that these materials are not toxic and suitable for cell growth.

CONCLUSIONS

In this study, the mechanical properties of dental resin can be improved by adding the β -Si₃N₄ whiskers. When the SiO₂ layers obtained by heating β -Si₃N₄ whiskers in air can uniformly distributed on the surface of β -Si₃N₄ whisker, the adhesion between the β -Si₃N₄ whisker and dental resin is very good. The mechanical properties of resin composites containing β -Si₃N₄ filler are significantly higher than those of pure resin. The flexural strength reaches the highest point of 139.8 MPa at the filler ratio of 50 wt %. The good adhesion also contributes to keep the flexural strength after hydrothermal cycling. The MTT absorbance results reveal that the resin composites containing Si₃N₄ filler are suitable for cell growth. Considering the biocompatibility and its favorable mechanical properties, the material may be a very promising candidate for high-stress dental restoration.

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REFERENCES

1. Tian, M.; Gao, Y.; Liu, Y.; Liao, Y. L. *Dent. Mater.* **2008**, *24*, 235.
2. Xu, H. H.; Quinn, J. B. *J. Biomed. Mater. Res.* **2001**, *58*, 81.
3. Bal, B.; Khandkar, A.; Lakshminarayanan, R.; Clarke, I.; Hoffman, A. A.; Rahaman, M. N. *J. Biomed. Mater. Res. Part B: Appl. Biomater.* **2008**, *87B*, 447.
4. Xu, H. H.; Martin, T. A.; Antonucci, J. M.; Eichmiller, F. C. *J. Dent. Res.* **1999**, *78*, 706.
5. Lawn, B. R. *Fracture of Brittle Solids*; Cambridge Univ Pr, New York, USA, **1993**.
6. Iwanaga, H.; Kawai, C. *J. Am. Ceram. Soc.* **1998**, *81*, 773.
7. Xu, H. H. *J. Dent. Res.* **1999**, *78*, 1304.
8. Xu, H. H.; Ostertag, C. P.; Braun, L. M.; Lloyd, I. K. *J. Am. Ceram. Soc.* **1994**, *77*, 1889.
9. Xu, H. H.; Eichmiller, F. C.; Smith, D. T.; Schumacher, G. E.; Giuseppetti, A. A.; Antonucci, J. M. *J. Mater. Sci.: Mater. Med.* **2002**, *13*, 875.
10. Amaral, M.; Costa, M. A.; Lopes, M. A.; Silva, R. F.; Santos, J. D.; Fernandes, M. H. *Biomaterials* **2002**, *23*, 4897.
11. Lu, L. M.; Zuo, K. H.; Zeng, Y. P. *J. Appl. Polym. Sci.* **2013**, *128*, 41.