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Dental resin composites containing silica-fused whiskers—effects of whisker-to-silica ratio on fracture toughness and indentation properties

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Abstract

Dental resin composites need to be strengthened in order to improve their performance in large stress-bearing applications such as crowns and multiple-unit restorations. Recently, silica-fused ceramic whiskers were used to reinforce dental composites, and the whisker-to-silica ratio was found to be a key microstructural parameter that determined the composite strength. The aim of this study was to further investigate the effects of whisker-to-silica ratio on the fracture toughness, elastic modulus, hardness and brittleness of the composite. Silica particles and silicon carbide whiskers were mixed at whisker : silica mass ratios of 0 : 1, 1 : 5, 1 : 2, 1 : 1, 2 : 1, 5 : 1, and 1 : 0. Each mixture was thermally fused, silanized and combined with a dental resin at a filler mass percentage of 60%. Fracture toughness was measured with a single-edge notched beam method. Elastic modulus and hardness were measured with a nano-indentation system. Whisker : silica ratio had significant effects on composite properties. The composite toughness (mean $\pm$ SD; $n = 9$) at whisker : silica = 2 : 1 was (2.47 ± 0.28) MPa $m^{1/2}$, significantly higher than (1.02 ± 0.23) at whisker : silica = 0 : 1, (1.13 ± 0.19) of a prosthetic composite control, and (0.95 ± 0.11) of an inlay/onlay composite control (Tukey's at family confidence coefficient = 0.95). Elastic modulus increased monotonically and hardness plateaued with increasing the whisker : silica ratio. Increasing the whisker : silica ratio also decreased the composite brittleness, which became about 1/3 of that of the inlay/onlay control. Electron microscopy revealed relatively flat fracture surfaces for the controls, but much rougher ones for the whisker composites, with fracture steps and whisker pullout contributing to toughness. The whiskers appeared to be well-bonded with the matrix, probably due to the fused silica producing rough whisker surfaces. Reinforcement with silica-fused whiskers resulted in novel dental composites that possessed fracture toughness two times higher than, and brittleness less than half of current dental composites.

Keywords: Dental resin composite; Reinforcement mechanisms; Whisker-to-silica ratio; Fracture toughness; Elastic modulus; Brittleness

1. Introduction

Extensive studies have been undertaken to understand and improve the microstructure and properties of dental resin composites [1–9]. Reinforcement with chopped glass fibers [10] and networked fibers [11], and optimization in filler level and degree of conversion [8,12–14] are among the experiments to improve the mechanical properties of resin composites. Other studies have investigated the effects of heat-curing or post-cure heat treatment on the enhancement of composite strength and toughness [5,12–20].

However, significant improvements are still needed in order to extend the use of dental resin composites to large stress-bearing applications such as direct posterior restorations involving cusps, and indirect crown and multiple-unit restorations. This is because the relatively high brittleness and low fracture resistance of current dental composites still limit their uses [21–23]. For example, a heat- and pressure-cured inlay/onlay

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composite had a relatively low flexural strength [24]. An indirect composite was not recommended for full crown applications due to its brittleness (Concept™ Processing Instructions, Ivoclar North America, Amherst, NY). For filled polymer crowns, fracture during service was observed and they have lost favor as they continued to fail [23]. Even for inlay applications, while the 7-year clinical failure rate of a composite for premolar inlays was relatively low, nearly half of the stress-bearing molar inlays had failed [25].

Recently, a novel ceramic whisker filler system was developed to reinforce dental composites [26,27]. The whiskers possessed high strength and fracture resistance, with sizes much smaller than chopped fibers. Silica glass particles were thermally fused onto the surfaces of the whiskers to facilitate silanization and to roughen the whisker surfaces for improved retention in the matrix. This method resulted in a two-fold increase in composite flexural strength compared to currently available dental resin composites [26,28]. A previous study [29] showed that the whisker-to-silica ratio was a key microstructural parameter that determined the strength of composites. However, that study focused on the processing of composites with different whisker : silica ratios and filler levels without investigating the changes in the fracture toughness of the composites. Furthermore, changes induced by whisker : silica ratio in the elastic modulus and hardness, which are important properties for dental composites and can be measured with indentation methods [30–32], are yet to be investigated.

While flexural and tensile tests yield results on deformation and fracture of the bulk specimens, indentation tests offer important information that is more relevant to applications that involve localized, non-uniform deformation or point contacts [33], such as dental occlusal contacts with surface asperities or third bodies during chewing and wear. The indentation method is especially useful when specimen dimensions are limited [30,31], such as tooth enamel or a restoration in a tooth preparation. Indentation can be used to characterize mechanical properties of restorative materials [34–37], and to probe the work-hardening inside small fatigued zones [38], which are difficult to quantify with bulk testing techniques. In addition, instrumented indentation techniques can continuously monitor loading–unloading during an indentation cycle. This process can provide information on the energy absorbed by the material during indentation [40] and the elastic modulus of the material [30–32,35].

The indentation hardness, H, can be used with fracture toughness, T, to yield the brittleness of the material, B, defined as [33]

$$B = H/T. \quad (1)$$

In restorative materials with the same fracture toughness, the material with a smaller hardness possesses a lower brittleness because it more readily yields under contact load, increasing the contact area to produce a smaller contact stress. For materials with the same hardness, the tougher material possesses a lower brittleness. With the unit of hardness being GPa and that of fracture toughness being $\mathrm{MPa\,m^{1/2}}$, the unit of brittleness is $\mathrm{GPa/MPa\,m^{1/2}}$. For simplicity, only the brittleness value is used with the unit of brittleness being omitted. As examples, the brittleness for a silicate glass is approximately 8 (highly brittle), and that for steel is about 0.1 (low brittleness) [33].

The aim of the present study, therefore, was to investigate the effect of whisker : silica ratio on the reinforcement of silica-fused whisker composites. It was hypothesized that the whisker : silica ratio would significantly influence the fracture toughness, elastic modulus, hardness, and brittleness of the whisker composites. It was further hypothesized that the whisker-reinforced composites would possess significantly higher fracture toughness and lower brittleness than the non-whisker control composites.

2. Materials and methods

2.1. Whisker : silica mixing, high temperature fusion, and silanization

The present study used silicon carbide whiskers (Advanced Refractory Technologies Buffalo, NY) having diameters ranging from 0.1 to 3 μm with a mean of approximately 0.9 μm, and lengths ranging from about 2 to 100 μm with a mean of 14 μm. The whiskers were mixed with silica having a nominal particle size of 0.04 μm (Aerosil OX50, Degussa Corp., Ridgefield, NJ) by dispersing and stirring in ethyl alcohol on a hot plate until dry [28]. Seven powders were thus obtained with the following whisker : silica mass ratios in the order of increasing whisker content: 0 : 1 (all silica, no whiskers), 1 : 5, 1 : 2, 1 : 1, 2 : 1, 5 : 1, and 1 : 0 (all whiskers). These ratios corresponded to whisker/(whisker + silica) mass percentages of 0%, 16.7%, 33.3%, 50%, 66.7%, 83.3%, and 100%, respectively. Each powder was heated in air for 30 min at a temperature of 800°C [41] in a modified Dicor™ furnace (Dentsply International, York, PA) with heating and cooling ramps of approximately 250°C/h. Each of the seven powders was then silanized by mixing it with 4% mass percentage of 3-methacryloxypropyltrimethoxysilane (MPTMS) and 2% *n*-propylamine in cyclohexane by means of a rotary evaporator under moderate vacuum in a 90°C water bath until dry.

2.2. Specimen fabrication

Each of the seven silanized powders was manually mixed by spatulation with a dental resin monomer

consisting of mass percentages of 48.965% of an oligomeric urethane derivative of Bis-GMA (NCO/Bis-GMA, Caulk/Dentsply, Milford, DE), 48.965% triethylene glycol dimethacrylate (TEGDMA), 2% benzoyl peroxide (BPO), and 0.07% 4-methoxylphenol (MEHQ). The paste was placed into a steel mold of 2 mm × 2 mm × 25 mm dimensions, both sides covered with mechanically clamped glass slides and heat-cured in an oven (Model 48, Fisher Scientific, Pittsburg, PA) at 140°C for 30 min at room atmospheric pressure to make flexural specimens. For each of the seven powders, a filler level mass percentage of 60% was used according to the results of a previous study [29].

Two control composites were also fabricated. Following the manufacturer's instructions, the paste of an indirect laboratory composite (Concept™, Ivoclar North America, Amherst, NY) was placed into the same molds and cured in the concept heat integrated processor at 120°C for 10 min under a pressure of 0.6 MPa. Concept™ consisted of a mass percentage of 76% silicate fillers in a urethanedimethacrylate resin (Technical Data Sheet, Ivoclar North America). It is denoted as "control c" in this paper. Following the manufacturer's instructions, the paste of a second indirect laboratory composite (Artglass™, Heraeus Kulzer GmbH, Wehrheim, Germany) was placed into the molds and cured in a Dentacolor XS™ photo-curing unit (Heraeus Kulzer GmbH, Wehrheim, Germany) for 90 s on each side of the specimen. According to the manufacturer, Artglass™ contained a mass percentage of 70% barium glass in a resin with tetra- and hexa-functional groups in addition to conventional bi-functional methacrylates. It is designated as "control a" in this article.

2.3. Testing

All the cured specimens were immersed in distilled water at 37°C for 24 h prior to testing. Fracture toughness was measured by using a single-edge-V-notched beam method [41]. A notch of a depth of approximately 500 μm was machined into each specimen by using a diamond blade of a thickness of 150 μm [37]. Diamond paste of 3 μm was then placed into the notch tip, and a sharp razor blade was used to further cut the notch to a total depth of about 800 μm. This method was demonstrated to produce relatively sharp notches, enabling a relatively accurate measurement of the fracture toughness [41]. The notch length and specimen dimensions were measured, and the notched specimen was fractured on a computer-controlled universal testing machine (model 5500R, Instron Corp., MA) in three-point flexure with a span of 10 mm at a crosshead speed of 1 mm/min, with the notch on the tensile side and the loading pin aligned with the notch. The fracture toughness was then calculated with the measured fracture load, specimen dimensions and notch depth using the single-edged-notched beam equations [41,42]. Nine specimens were tested for each of the nine materials (seven whisker composites and two controls). The specimens were tested in air at a relative humidity of about 50% and a temperature of 22°C.

A nano-indentation system (Nano Instruments, Knoxville, TN) with a diamond Berkovich indenter, which is a three-sided pyramid with the same depth-to-projected area ratio as the Vickers indenter [39], was used to produce indentations. The indentation loads and the corresponding displacements were recorded continuously throughout a loading-unloading cycle, enabling the measurement of the elastic modulus of the indented specimen. The calculation of hardness and elastic modulus was made according to a method described previously [30]. The method involves the extrapolation of a tangent to the top of the unloading curve to determine the depth (a combination of elastic and plastic displacement) over which the indenter tip is in contact with the specimen at the maximum load, P_{max}. This depth, and the knowledge of the indenter geometry, gives the contact area, A; hardness then follows directly from [30,32]

$$H = P_{max}/A. \tag{2}$$

The slope of the unloading curve also provides a measure of the contact stiffness, which can be used with the contact area to determine the elastic modulus. The elastic modulus obtained, sometimes referred to as the indentation modulus, E, is related to the Young's modulus E_Y by [30,32]

$$E = E_Y/(1 - v^2), \tag{3}$$

where v is Poisson's ratio. E_Y can be obtained via Eq. (3) for materials with known v For materials with v of approximately 0.25 [32], $E_Y = 0.94E$. The present study measured indentation modulus E, without trying to calculate E_Y.

Six different specimens were indented for each material, with four indents approximately 1 mm apart in each specimen for a total of 24 indentation for each material. P_{max} of 1 N was used [37] to yield indentation contact areas large enough to represent the composite, rather than the individual filler particles or the resin phase in between the filler particles.

Selected filler powders and specimen fracture surfaces were sputter-coated with gold and examined with a scanning electron microscope (SEM, model JSM-5300, JEOL, Peabody, MA). One-way ANOVA was performed to detect significant difference ($\alpha = 0.05$) in properties. Tukey's and Dunn's multiple comparison methods were used at a family confidence coefficient of 0.95 to compare the measured values.

3. Results

SEM micrographs in Fig. 1 show (A) as-received whiskers, (B) a higher magnification of the surface of a typical as-received whisker, and (C) the surface of a whisker fused with silica particles. Some of the as-received silicon carbide whiskers were not straight (arrows in (A)), the diameter of many whiskers appeared to vary along their length, and the whisker surface appeared relatively smooth (arrow in (B)). Silica particles were observed on the surfaces of whiskers after fusion at 800°C for 30 min (arrows in (C)). The whisker : silica ratio for Fig. 1C was 2 : 1.

Fig. 2 plots the fracture toughness of whisker composites as a function of whisker : silica ratio, along with the two controls. Increasing the whisker : silica ratio from 0 : 1 (all silica) to 2 : 1 resulted in a significant increase (one-way ANOVA; $p<0.001$) in the measured fracture toughness; the toughness then plateaued when the whisker : silica ratio was further increased to 1 : 0 (all whisker). The fracture toughness values (mean $\pm$ SD; $n=9$) at whisker : silica = 2 : 1, 5 : 1 and 1 : 0 were $(2.47\pm0.28)\,\mathrm{MPa\,m^{1/2}}$, $(2.28\pm0.18)\,\mathrm{MPa\,m^{1/2}}$ and $(2.30\pm0.13)\,\mathrm{MPa\,m^{1/2}}$, respectively, not significantly different from each other (Tukey's multiple comparison test; family confidence coefficient = 0.95). All of them were significantly higher than $(1.02\pm0.23)\,\mathrm{MPa\,m^{1/2}}$ at whisker : silica = 0 : 1 (all silica), $(1.13\pm0.19)\,\mathrm{MPa\,m^{1/2}}$ for control a (Artglass™), and $(0.95\pm0.11)\,\mathrm{MPa\,m^{1/2}}$ for control c (Concept™) (Tukey's multiple comparison test; family confidence coefficient = 0.95).

The composite elastic modulus and hardness measured by nano-indentation are plotted in Fig. 3. Increasing the whisker : silica ratio monotonically significantly increased the elastic modulus (Kruskal–Wallis one-way ANOVA; $p<0.001$). The composite modulus values at whisker : silica ratios from 2 : 1 to 1 : 0 were significantly higher than those from 0 : 1 to 1 : 1; those at 1 : 2 and 1 : 1 were significantly higher than that at 0 : 1 (Dunn's multiple comparison test; family confidence coefficient = 0.95). On the other hand, the magnitude of change in the hardness of whisker composites was relatively small (Fig. 3B) compared to that in elastic modulus (Fig. 3A), although the variations were still statistically significant. Controls a and c had similar elastic modulus values, but the hardness of control c is significantly higher than that of control a ($p<0.05$; Student's t).

The composite brittleness values were calculated using Eq. (1) and are plotted in Fig. 4. With increasing whisker: silica ratio, the brittleness of whisker composites steadily decreased, from (0.73 ± 0.20) at whisker : silica = 0 : 1 (all silica) to (0.29 ± 0.06) at 1 : 0. Control a had a brittleness of (0.51 ± 0.13), while that of control c was (1.03 ± 0.24), nearly three times higher than those of the whisker composites at whisker : silica ratios from 2 : 1 to 1 : 0.

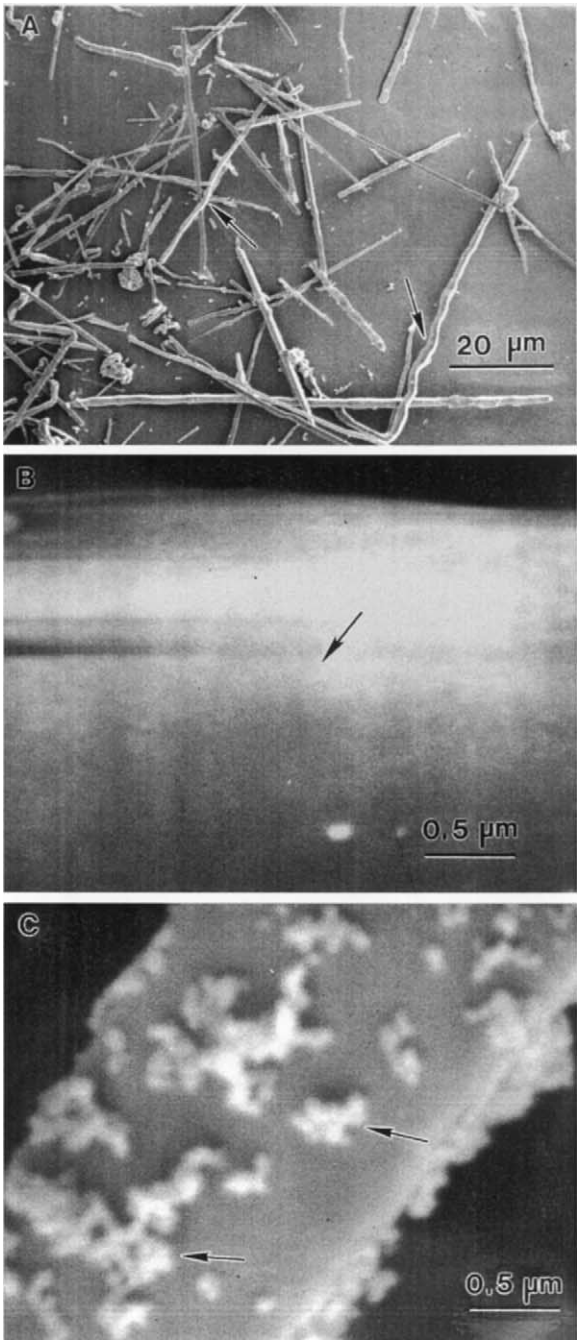

Fig. 1. SEM micrographs show (A) as-received whiskers, (B) a higher magnification of the surface of an as-received whisker, and (C) the surface of a whisker fused with silica particles. Some whiskers were not straight (arrows in (A)), the diameter of many whiskers appeared to vary along their length, and the whisker surface appeared relatively smooth (arrow in (B)). Silica particles were observed on the surfaces of whiskers after fusion at 800°C (arrows in (C)). The whisker : silica ratio for Fig. 1C was 2 : 1.

SEM micrographs of fracture surfaces are shown in Fig. 5 for (A) control c, (B) control a, (C) whisker composite at whisker : silica = 2 : 1, and (D) whisker composite at whisker : silica = 5 : 1 at a higher

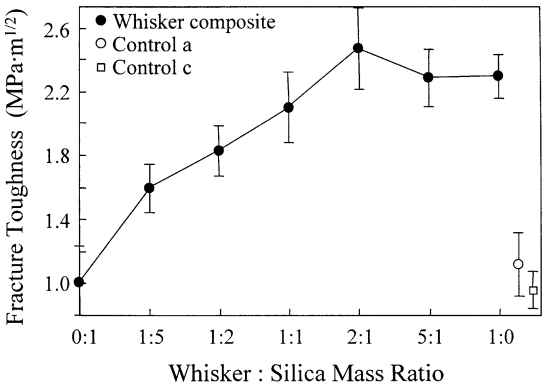

Fig. 2. Fracture toughness of whisker composites as a function of whisker : silica ratio, along with control a (Artglass™) and control c (Concept™). Each datum is the mean with the error bar showing one standard deviation (SD), $n = 9$.

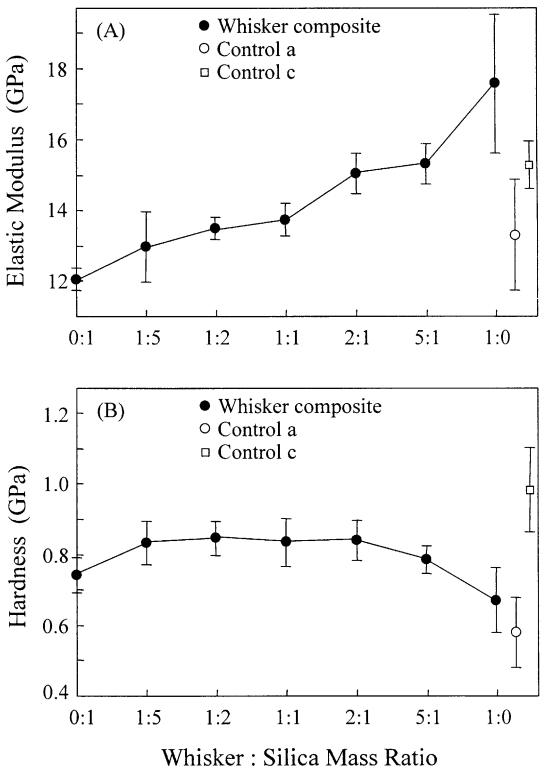

Fig. 3. The composite elastic modulus and hardness measured by nano-indentation. Each datum is the mean with the error bar showing one SD, $n = 6$.

magnification. The two controls had relatively flat fracture surfaces, similar to that of the composite at whisker : silica of 0 : 1 (all silica). The composites containing silica-fused whiskers had much rougher fracture surfaces, an example of which is shown in (C), with large fracture steps (large arrow in (C)) and pulled-out whiskers (small arrows). The whiskers appeared to be well bonded with the matrix resin at the whisker–resin interfaces, as indicated by the arrows in (D).

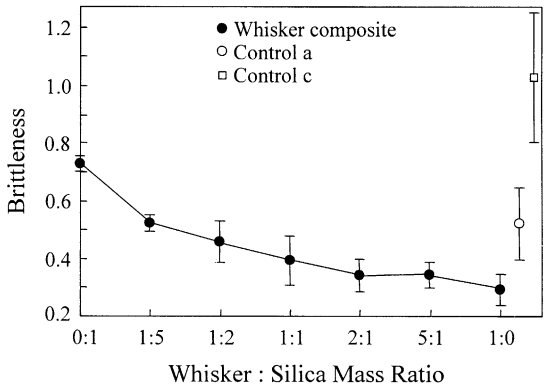

Fig. 4. The composite brittleness values were calculated using Eq. (1). Increasing the whisker : silica ratio decreased the brittleness of composite. The whisker composites had lower brittleness than control c.

4. Discussion

Reinforcement of dental composites with silica-fused whiskers resulted in a two-fold increase in fracture toughness. The whisker : silica ratio in producing the silica-fused whisker fillers played a critical role in determining the composite properties. The composite at whisker : silica = 0 : 1 (all silica) behaved as a typical conventional composite filled with glass particles, having fracture-surface features and a mean fracture toughness value similar to those of the commercial control composites. Higher whisker : silica ratios with increased whisker content in the composite rapidly increased the fracture toughness. During composite cracking, whiskers and fibers in the composite have been observed to pin and deflect the crack propagation, thus significantly increasing the roughness of fracture surfaces by creating steps and tortuous topographies [28,43]. A typical fracture step is shown in Fig. 5C and appears to be a direct result of the deflection of the crack to another plane in the composite. These features constitute a high surface area, consuming energy in creating new surfaces [33]. Enamel rods in teeth were observed to behave in a similar way by deflecting and resisting crack propagation [32]. Furthermore, when intercepting a crack, the elongated whiskers bridge the crack and resist it from opening and propagating, thus exerting a closure force on the crack, thereby reducing the net stress intensity at the crack tip [33,43,44].

Therefore, the increased whisker content in the composite appeared to enhance these toughening mechanisms, which may explain the observed increase in toughness when the whisker : silica ratio was increased from 0 : 1 to 2 : 1. However, when the whisker : silica ratio was further increased to 1 : 0, the toughness plateaued (Fig. 2). This is likely because the toughness increase from a higher whisker content may be offset by whisker entanglement and agglomeration at a high

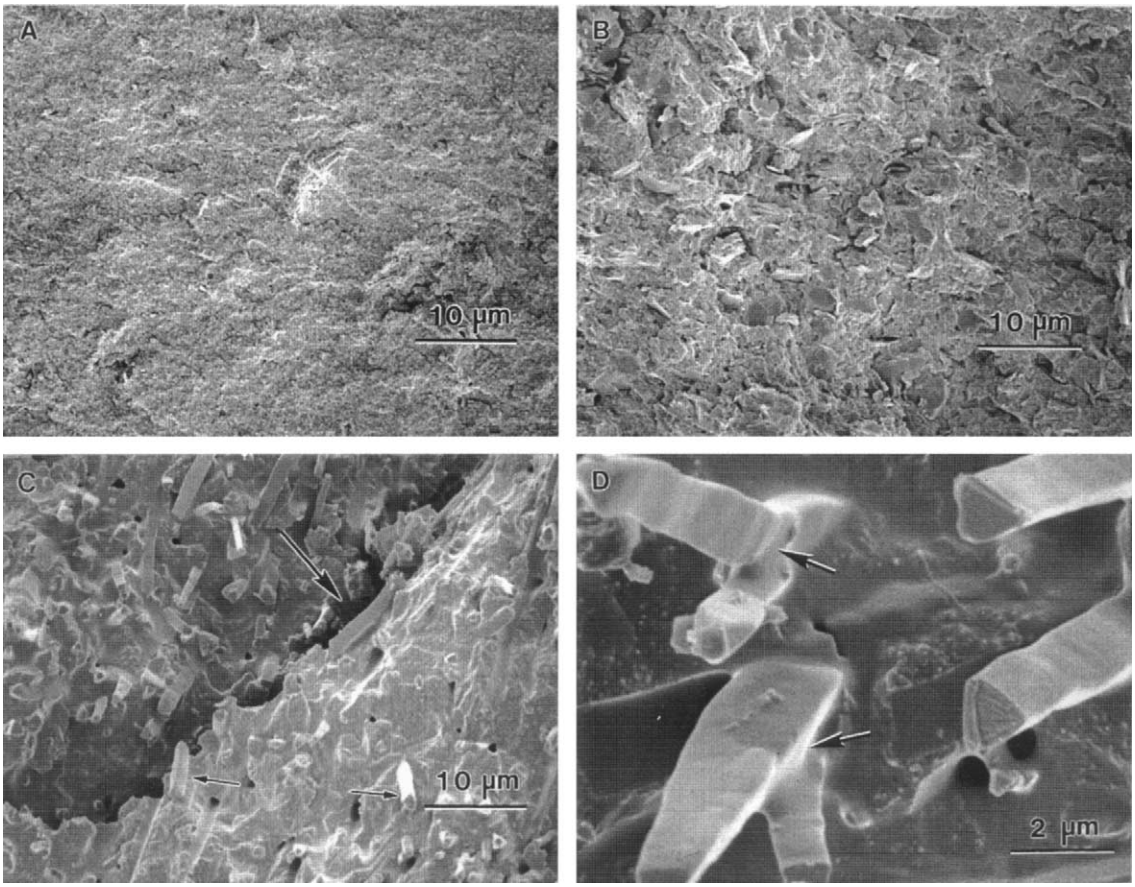

Fig. 5. SEM micrographs of fracture surfaces for (A) control c, (B) control a, (C) whisker composite at whisker : silica = 2 : 1, and (D) whisker composite at whisker : silica = 5 : 1 at a higher magnification. The two controls had relatively flat fracture surfaces, similar to that of the composite at whisker : silica of 0 : 1 (all silica). The composites containing silica-fused whiskers had much rougher fracture surfaces (C), with large fracture steps (large arrow in (C)) and pulled-out whiskers (small arrows). The whiskers appeared to be well bonded with the matrix resin at the whisker–resin interfaces, as indicated by the arrows in (D).

whisker content, especially at whisker : silica of 1 : 0 (all whiskers, no silica). A major problem encountered in the whisker reinforcement technology is that the highly elongated whiskers easily entangle and "ball up" during mixing [45,46]. In our previous study [29] using only whiskers without mixing with silica particles, SEM observations showed whisker entanglement in the composite, consistent with previous observations that these whiskers easily entangled and were difficult to separate from each other and disperse in the matrix [45,46]. The fine silica particles appeared to get in between the whiskers separating the whiskers from each other, thereby minimizing whisker entanglement. Therefore, mixing and fusing silica particles with whiskers not only enhanced the whisker silanization and bonding to the resin matrix, but also improved whisker distribution in the matrix, both factors contributing to the measured substantial increase in the composite fracture toughness.

It is interesting to compare the dependence of fracture toughness on the whisker : silica ratio with that of the flexural strength. Flexural strength was measured in a previous study [29] and replotted here in Fig. 6; it increased with whisker : silica ratio up to 5 : 1, and then decreased sharply when the ratio was further increased

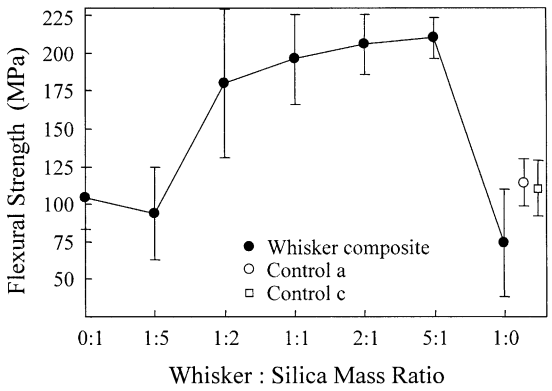

Fig. 6. The flexural strength of composite increased with whisker : silica ratio up to 5 : 1, and then decreased rapidly at a ratio of 1 : 0 (all whiskers). Values for controls a (Artglass™) and c (Concept™) are also shown. Each datum is the mean with the error bar showing one SD, $n = 6$.

to 1 : 0 (all whiskers). In contrast, the fracture toughness plateaued and did not decrease at 1 : 0. The composite strength is determined by the intrinsic flaws (surface and volume flaws) in the specimen, such as pores and filler agglomerates. On the other hand, the fracture toughness is dependent on the material's resistance to crack propagation, often measured using specimens with notches machined into them. The notch, which was about 800 μm long in this study, was likely much larger than the intrinsic flaws in the specimen. Therefore, the strength of specimens without notches at whisker : silica of 1 : 0 (all whiskers, no silica) decreased because of strength-controlling flaws from the observed whisker agglomeration at whisker : silica of 1 : 0 [29]. The fracture toughness at whisker :silica of 1 : 0, on the other hand, was not lower than those at other whisker : silica ratios, because the other specimens also had the large controlling flaw—the notch. This appears to suggest that while fracture toughness of notched specimens provides useful information, the strength of materials without artificial notches should also be characterized to obtain a more complete view, because most in vivo restorations and implants are without notches machined into them.

While the elastic modulus of the whisker composites increased monotonically with the whisker : silica ratio, the composite hardness was less sensitive to this ratio. The modulus is the material's resistance to elastic deformation; the hardness is the material's resistance to local plastic deformation. The mean modulus of the whisker composite at a whisker : silica of 1 : 0 was 17.6 GPa, slightly higher than 15.3 GPa and 13.3 GPa of the two controls, but still lower than 22 GPa of human tooth dentin [32]. The hardness values of the whisker composites are in between those of controls a and c. While this would suggest that the whisker composites should not cause excessive wear of the opposing enamel, actual wear studies are needed to verify this. In addition, the hardness enabled the calculation of the composite brittleness, or the ratio of hardness/fracture toughness, which serves as a useful parameter in comparing the brittleness of materials [33]. For microstructural design of new restorative materials with reduced brittleness, efforts should be focused on increasing the toughness more than increasing the hardness. This is because increasing the hardness more than increasing the toughness only yields a more brittle material. It should be noted that there are other definitions of brittleness, e.g., $B = EH/K_{IC}^2$, where K_{IC} is critical stress intensity factor; it has been proposed based on deformation and fracture energy ratio [47]. Using this equation, the trend of brittleness versus whisker : silica ratio and the ranking of materials' brittleness will be similar to those in Fig. 4.

In summary, reinforcement with silica-fused whiskers resulted in novel dental composites that possessed fracture toughness two times higher than, and brittleness less than half of, those of currently available indirect dental composites. Composite elastic modulus increased monotonically with the whisker : silica ratio, while hardness was less sensitive to this microstructural parameter. SEM examinations suggested toughening mechanisms as crack deflection and bridging by, and frictional pullout of, the silica-fused whiskers in the composites. The results of this study suggest that mixing silica particles with the highly elongated whiskers minimized whisker entanglement and improved distribution of fillers in the matrix. In addition, the fusion of silica glass particles onto the whiskers not only facilitated the whisker silanization and bonding with the resin matrix, but also enhanced the whisker retention in the matrix by providing rougher whisker surfaces. These factors together produced dental resin composites with superior fracture toughness and low brittleness.

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Disclaimer

Certain commercial materials and equipment are identified to specify the experimental procedure. Such identification does not imply endorsement by NIST or ADAHF or that the material or equipment identified is necessarily the best available for the purpose.

References

[1] Bowen RL. Properties of a silica-reinforced polymer for dental restorations. J Am Dent Assoc 1963;66:57–64.
[2] Calais JG, Söderholm KJM. Influence of filler type and water exposure on flexural strength of experimental composite resins. J Dent Res 1988;67:836–40.
[3] Willems G, Lambrechts P, Braem M, Celis JP, Vanherle G. A classification of dental composites according to their morphological and mechanical characteristics. Dent Mater 1992;8:310–9.
[4] Anusavice KJ. Challenges to the development of esthetic alternatives to dental amalgam in an academic research center. Acad Dent Mater Trans 1996;9:25–50.
[5] Rueggeberg FA, Ergle JW, Lockwood PE. Effect of photoinitiator level on properties of a light-cured and post-cure heated model resin system. Dent Mater 1997;13:360–4.
[6] Eick JD, Kaufman GM, Chappelow CC. Applications of polymers: what are the future trends? Acad Dent Mater Trans 1997;10:89–98.
[7] Bayne SC, Thompson JY, Swift Jr EJ, Stamatiades P, Wilkerson M. A characterization of first-generation flowable composites. J Am Dent Assoc 1998;129:567–77.

[8] Ferracane JL, Berge HX, Condon JR. In vitro aging of dental composites in water—effect of degree of conversion, filler volume, and filler/matrix coupling. J Biomed Mater Res 1998;42: 465–72.
[9] Watts DC, Hindi AA. Intrinsic soft-start polymerization shrinkage-kinetics in an acrylate-based resin composite. Dent Mater 1999;15:39–45.
[10] Krause WR, Park SH, Straup RA. Mechanical properties of Bis-GMA resin short glass fiber composites. J Biomed Mat Res 1989;23:1195–211.
[11] Bayne SC, Thompson JY. Mechanical property analysis of two admixed PRIMM-modified commercial dental composites. Acad Dent Mater Trans 1996;9:238.
[12] Ferracane JL, Condon JR. Post-cure heat treatments for composites: properties and fractography. Dent Mater 1992;8:290–5.
[13] Ferracane JL, Hopkin JK, Condon JR. Properties of heat-treated composites after aging in water. Dent Mater 1995;11: 354–8.
[14] Loza-Herrero MA, Rueggeberg FA, Caughman WF, Schuster GS, Lefebvre CA, Gardner FM. Effect of heating delay on conversion and strength of a post-cured resin composite. J Dent Res 1998;77:426–31.
[15] Wendt SL. The effect of heat as a secondary cure upon the physical properties of three composite resins: I. Diametral tensile strength, compressive strength and marginal dimensional stability. Quintessence Int 1987;18:265–71.
[16] Wendt SL, Leinfelder KF. The clinical evaluation of heat-treated composite resin inlays. J Am Dent Assoc 1990;120:177–81.
[17] Asmussen E, Peutzfeldt A. Mechanical properties of heat-treated restorative resin for use in the inlay/onlay technique. Scand J Dent Res 1990;98:564–7.
[18] McCabe JF, Kagi S. Mechanical properties of a composite inlay material following post-curing. Br Dent J 1991;171:246–8.
[19] Covey DA, Tahaney SR, Davenport JM. Mechanical properties of heat-treated composite resin restorative materials. J Prosthet Dent 1992;68:458–61.
[20] Hirabayashi S, Hood JAA, Hirasawa T. The extent of polymerization of class II light-cured composite resin restorations: effects of increment placement technique, exposure time and heating for resin inlays. Dent Mater J 1993;12:159–70.
[21] Sakaguchi RL, Cross M, Douglas WH. A simple model of crack propagation in dental restorations. Dent Mater 1992;8:131–6.
[22] Wilder Jr AD, Bayne SC, Heymann HO. Long-term clinical performance of direct posterior composites. Acad Dent Mater Trans 1996;9:151–69.
[23] Christensen GJ. Porcelain-fused-to-metal vs. nonmetal crowns. J Am Dent Assoc 1999;130:409–11.
[24] Drummond JL, Savers EE. In vitro aging of a heat/pressure-cured composite. Dent Mater 1993;9:214–6.
[25] Donly KJ, Jensen ME, Triolo P, Chan D. Clinical comparison of resin composite inlay and onlay posterior restorations and cast-gold restorations at 7 years. Quintessence Int 1999;30: 163–9.
[26] Xu HHK, Martin TA, Antonucci JM, Eichmiller FC. Ceramic whisker reinforcement of dental resin composites. J Dent Res 1999;78:706–12.
[27] Xu HHK, Eichmiller FC. Reinforcement of dental and other composite materials. US Patent No. 5,861,445, 1999.
[28] Xu HHK. Dental composite resins containing silica-fused ceramic single-crystalline whiskers with various filler levels. J Dent Res 1999;78:1304–11.
[29] Xu HHK, Quinn JB, Giuseppetti AA, Eichmiller FC. Effects of whisker-to-silica ratio on the reinforcement of dental resin composites with silica-fused whiskers. J Dent Res 2000;79:1844–9.
[30] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J Mater Res 1992;7:1564–83.
[31] Willems G, Celis JP, Lambrechts P, Braem M, Vanherle G. Hardness and Young modulus determined by nanoindentation technique of filler particles of dental restorative materials compared with human enamel. J Biomed Mater Res 1993;27: 747–55.
[32] Xu HHK, Smith DT, Jahanmir S, Romberg E, Kelly JR, Thompson VP, Rekow ED. Indentation damage and mechanical properties of human enamel and dentin. J Dent Res 1998;77: 472–80.
[33] Lawn BR. Fracture of brittle solids. London: Cambridge University Press, 1993 (ch 8).
[34] Ferracane JL. Indentation fracture toughness testing and crack propagation mode in dental composites. Mater Res Soc Symp Proc 1989;110:619–24.
[35] Van Meerbeek B, Willems G, Celis JP, Roos JR, Braem M, Lambrechts P, Vanherle G. Assessment by nano-indentation of the hardness and elasticity of the resin-dentin bonding area. J Dent Res 1993;72:1434–42.
[36] Peterson IM, Pajares A, Lawn BR, Thompson VP, Rekow ED. Mechanical characterization of dental ceramics by Hertzian contacts. J Dent Res 1998;77:589–602.
[37] Xu HHK, Smith DT, Schumacher GE, Eichmiller FC, Antonucci JM. Indentation modulus and hardness of whisker-reinforced heat-cured dental resin composites. Dent Mater 2000;16:248–54.
[38] Xu HHK, Eichmiller FC, Giuseppetti AA, Johnson CE. Cyclic contact fatigue of a silver alternative to amalgam. Dent Mater 1998;14:11–20.
[39] Xu HHK, Smith DT, Jahanmir S. Influence of microstructure on indentation and machining of dental glass-ceramics. J Mater Res 1996;11:2325–37.
[40] Xu HHK. Whisker-reinforced heat-cured dental resin composites: effects of filler level and heat-cured temperature and time. J Dent Res 2000;79:1392–7.
[41] The Versailles Project on Advanced Materials and Standards (VAMAS) and The European Structural Integrity Society (ESIS). Fracture toughness of ceramics using the SEVNB method; round robin. Swiss Federal Laboratories for Materials Testing and Research, 1999.
[42] American Society for Testing and Materials. Standard test methods for determination of fracture toughness of advanced ceramics at ambient temperatures. West Conshohochen, PA, ASTM C1421-99, 1999.
[43] Xu HHK, Ostertag CP, Braun LM, Lloyd IK. Short-crack mechanical properties and failure mechanisms of Si_3N_4-matrix/SiC-fiber composites. J Am Ceram Soc 1994;77:1889–96.
[44] Xu HHK, Jahanmir S, Ives LK, Job LS, Ritchie KT. Short-crack toughness and abrasive machining of silicon nitride. J Am Ceram Soc 1996;79:3055–64.
[45] Hood PE, Pickers JO. Silicon carbide whisker composites. US Patent 4,463,058, 1984.
[46] Hirata Y, Matsushita S, Nakagama S, Ishihara Y, Hori S. Rheological properties and consolidation of the suspension in the alumina powder-silicon nitride whisker system. J Ceram Soc Jpn 1989;97:866–71.
[47] Quinn JB, Quinn GD. Indentation brittleness of ceramics: a fresh approach. J Mater Sci 1997;32:4331–46.