

Dental resin composites containing ceramic whiskers and precured glass ionomer particles

H.H.K. Xu^{a,*}, F.C. Eichmiller^a, J.M. Antonucci^b, G.E. Schumacher^a, L.K. Ives^b

^aPaffenbarger Research Center, American Dental Association Health Foundation, Building 224, Room A-153, Gaithersburg, MD 20899-8546, USA

^bNational Institute of Standards and Technology, Gaithersburg, MD 20899-8546, USA

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Abstract

Objectives: Glass ionomer, resin-modified glass ionomer, and compomer materials are susceptible to brittle fracture and are inadequate for use in large stress-bearing posterior restorations. The aim of this study was to use ceramic single crystal whiskers to reinforce composites formulated with precured glass ionomer, and to examine the effects of whisker-to-precured glass ionomer mass ratio on mechanical properties, fluoride release, and polishability of the composites.

Methods: Silica particles were fused onto silicon nitride whiskers to facilitate silanization and to improve whisker retention in the matrix. Hardened glass ionomer was ground into a fine powder, mixed with whiskers, and used as fillers for a dental resin. Four control materials were also tested: a glass ionomer, a resin-modified glass ionomer, a compomer, and a hybrid composite. A three-point flexural test was used to measure flexural strength, modulus, and work-of-fracture. A fluoride ion-selective electrode was used to measure fluoride release. Composite surfaces polished simulating clinical procedures were examined by SEM and profilometry.

Results: At whisker/(whisker + precured glass ionomer) mass fractions of 1.0 and 0.91, the whisker composite had a flexural strength in MPa (mean (SD); $n = 6$) of (196 (10)) and (150 (16)), respectively, compared to (15 (7)) for glass ionomer, (39 (8)) for resin-modified glass ionomer, (89 (18)) for compomer, and (120 (16)) for hybrid composite. The whisker composite had a cumulative fluoride release of nearly 20% of that of the glass ionomer after 90 days. The whisker composites had surface roughness comparable to the hybrid resin composite.

Significance: Composites filled with precured glass ionomer particles and whiskers exhibit moderate fluoride release with improved mechanical properties; the whisker-to-glass ionomer ratio is a key microstructural parameter that controls fluoride release and mechanical properties. Published by Elsevier Science Ltd on behalf of Academy of Dental Materials.

Keywords: Ceramic whisker; Glass ionomer; Reinforcement; Resin composite; Strength; Fluoride

1. Introduction

Resin composites are generally composed of silanized particulate silicate glass fillers in a polymeric matrix derived from the polymerization of a mixture of methacrylate monomers. Considerable efforts have been devoted to the improvement of resin composites, including improvement in filler packing, optimization in filler levels, and development of hybrid filler phases [1–8]. Besides silicate glass particles, chopped glass fibers [9] and porous networks of fibers [10] have also been incorporated as fillers into dental composites. These improvements have not been sufficient to merit recommendation that direct-filling resin composites

be used for large stress-bearing posterior restorations, especially those that involve cusp replacements where large stresses can be generated during mastication [11,12].

Recently, ceramic single crystal whiskers were described as fillers to reinforce dental resin composites [13]. Silica particles were fused onto the individual whiskers to facilitate whisker silanization, to minimize whisker entanglement by facilitating their dispersion, and to enhance whisker retention in the matrix by providing roughness on the whisker surfaces [14]. The ceramic whiskers are single crystals possessing a high degree of structural perfection and, hence, superior strength and toughness values. For example, the tensile strength of ceramic silicon nitride whiskers is approximately 50 GPa, compared to approximately 3 GPa for glass fibers and 0.1 GPa for bulk glass [15–17]. The fracture toughness of silicon nitride is nearly 3 MPa·m^{1/2}, while that of glass is approximately

* Corresponding author. Tel.: + 1-301-975-6804; fax: + 1-301-963-9143.

E-mail address: hockin.xu@nist.gov (H.H.K. Xu).

0.7 MPa·m^{1/2}. In addition, the shape of the whiskers is highly elongated (e.g. a diameter of 0.5 μm and a length of 5 μm) with the potential benefit of bridging matrix microcracks and preventing them from propagating [15,18,19], as well as providing resistance to dislodgment from the matrix during wear processes. A recent study [13] has shown that ceramic whisker reinforcement imparted a nearly two-fold increase in the flexural strength and fracture toughness of dental resin composites. The present study will extend this concept by attempting to formulate a whisker-reinforced composite that releases fluoride.

It has been reported that approximately half of all restorative dentistry involved the replacement of existing restorations, and about 40% of all such replacements were attributed to recurrent caries [20]. The sustained release of small amounts of fluoride could provide a substantial advantage for a dental restoration if the fluoride could enrich neighboring enamel or dentin to combat secondary caries [21–26]. Glass ionomer [27–29] and resin-modified glass ionomer materials [30–32] have received much attention due to their significant release of fluoride, the uptake of fluoride in adjacent cavity walls and plaque, and the enhanced reprecipitation of calcium and phosphate promoted by the fluoride release [21,24,33–36]. However, the inferior mechanical properties of glass ionomer and subsequent resin-modified glass ionomer materials have limited their use [28,37–40]. Although ameliorating some problems of conventional glass ionomers, resin-modified versions have not achieved sufficient strength for use in large stress-bearing restoration [41]. It was predicted that for these materials, “the most intractable problem is likely to be lack of strength and toughness” [42].

The aim of the present study, therefore, was to combine the fluoride release of glass ionomer with the superior strength of whiskers, to develop resin composites reinforced with a novel filler system that comprised a mixture of ceramic whiskers and precured glass ionomer particles, and to investigate the effects of whisker-to-precured glass ionomer ratio on mechanical properties, fluoride release, and polishability of the composites. It was hypothesized that while the precured glass ionomer fillers in the composite would release fluoride, the whisker fillers in the composite would provide the needed mechanical strength. It was further hypothesized that the composite mechanical properties and fluoride release could be tailored by varying a key microstructural parameter: the whisker-to-glass ionomer filler ratio. Four control materials with varying fluoride release and flexural strength were also tested for comparison.

2. Materials and methods

2.1. Filler powder preparation

Ceramic silicon nitride (β-Si₃N₄) single crystal whiskers (UBE Industries, New York, NY) with diameters ranging

from 0.1 to 1.5 μm (mean = 0.4 μm) and lengths ranging from 2 to 20 μm (mean = 5 μm) were mixed with fumed silica having a nominal particle size of 0.04 μm (Aerosil OX50, Degussa Corp., Ridgefield, NJ). A whisker:silica mass ratio of 2:1 was used and the mixture was dispersed by stirring in ethyl alcohol with a magnetic stir bar under moderate vacuum until dry [13]. The silica particles were fused onto the surfaces of whiskers to facilitate silanization and to roughen the whisker surfaces for enhanced retention in the matrix. To fuse the silica particles onto the whiskers, the dried mixture was heated in air for 30 min at a temperature of 800°C [13]. The heat-treated powder was silanized by mixing it with mass fractions of 4% 3-methacryloxypropyltrimethoxysilane (MPTMS) and 2% *n*-propylamine in cyclohexane by means of a rotary evaporator at room temperature for 30 min and then in a 90°C water bath under a moderate vacuum until dry.

The powder and liquid components of a conventional glass ionomer (Ketac™-Bond, batch # 050790, ESPE, Germany) were mixed according to the manufacturer's instructions, and placed into steel molds, 2 × 2 × 20 mm, to make specimens. The open sides of the mold were covered with mylar strips mechanically clamped between glass slides, and the entire assembly was incubated in a 100% humidity humidior at 37°C for 24 h. The specimens were then demolded and manually ground in a mortar with a pestle into a fine powder of a particle size ranging from approximately 0.5 to 5 μm, with a mean of approximately 1 μm. This cured, ground glass ionomer cement powder will be referred to as “precured glass ionomer powder” or “gi”. The powder was silanized using the same procedure as described for the silica-fused whiskers.

2.2. Specimen fabrication

The silanized whiskers and precured glass ionomer powders were manually blended by spatulation into 6 fillers with whisker:precured glass ionomer mass ratios of 0:1, 1:4, 1:1, 4:1, 10:1, and 1:0. These corresponded to mass fractions of whisker/(whisker + precured glass ionomer powder), or w/(w + gi), of 0, 20, 50, 80, 91, and 100%, respectively. These mass fractions corresponded to volume fractions of approximately 0, 10, 37, 70, 85, and 100%, respectively. Each filler was manually blended by spatulation with a resin monomer consisting of mass fractions of 48.975% Bis-GMA, 48.975% triethylene glycol dimethacrylate (TEGDMA), 0.05% 2,6-di-*tert*-butyl-4-methylphenol (BHT), and 2% benzoyl peroxide (BPO) to form the initiator paste of a two-part chemically activated composite. The accelerator paste consisted of the same amount of filler mixed with a resin made of mass fractions of 49.5% Bis-GMA, 49.5% TEGDMA, and 1% *N,N*-dihydroxyethyl-*p*-toluidine (DHEPT) as the polymerization accelerator. A total filler mass fraction of 55% was used for all the whisker composites [13]. For preparation of the flexural specimens, equal masses of the two pastes were manually blended by

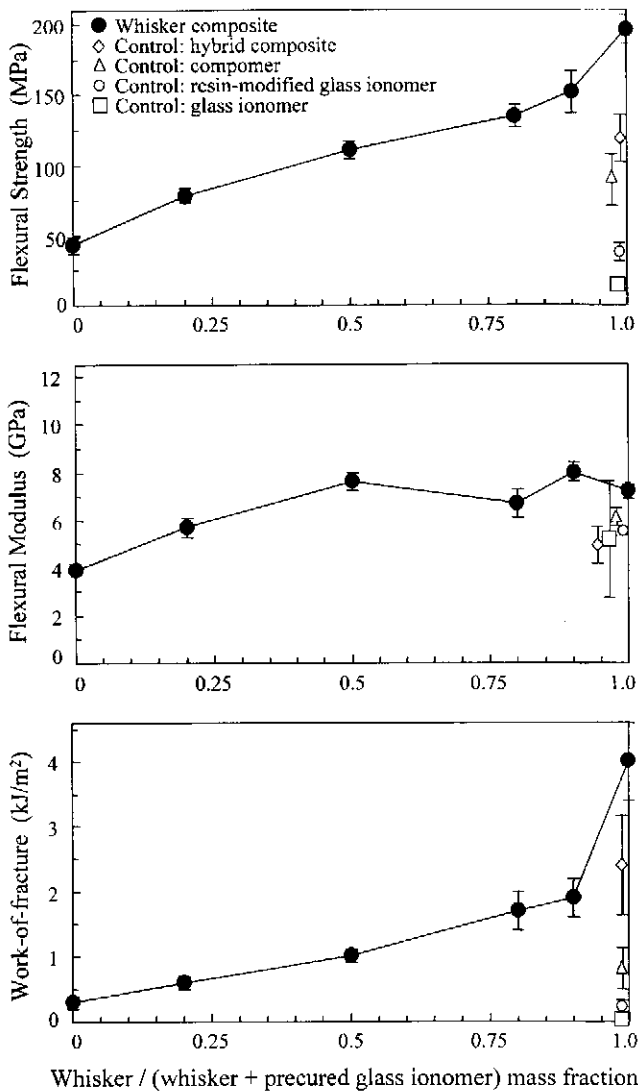


Fig. 1. Mechanical properties of the composites filled with whiskers and precured glass ionomer particles as a function of whisker/(whisker + precured glass ionomer) mass fraction.

spatulation and then placed into molds of $2 \times 2 \times 20$ mm. The paste hardened in approximately 2 min. For measurement of fluoride release, specimens of $2 \times 2 \times 8$ mm were made in the same manner. Each whisker specimen was allowed to incubate in the mold kept in an oven at 37°C for 15 min and then demolded. The flexural specimens were then immersed in distilled water at 37°C for 24 h prior to flexural testing.

Four control materials were selected to represent a range of strength and fluoride release. A glass ionomer (Ketac™-Bond, batch # 050790, ESPE, Germany) was mixed and cured as described previously. A resin-modified glass ionomer (Vitremmer™, batch # 19931105, 3M, St. Paul, MN) was mixed according to the manufacturer's instructions, placed into molds of $2 \times 2 \times 20$ mm, and cured using visible light (Triad 2000, Dentsply International, Inc., York, PA) for 1 min on each side of the specimen. Similarly, a compomer

(Dyract™, batch # 9501182, Caulk/Dentsply, Inc., Milford, DE) was mixed according to the manufacturer's instructions, placed into molds and light-cured for 1 min on each side of the specimen. In addition, a hybrid resin composite (TPH™, batch # 9607081, Caulk/Dentsply, Inc., Milford, DE), consisting of silicate particles of about $0.8 \mu\text{m}$ in diameter at a filler level of 78% mass fraction in a matrix resin of a urethane-modified Bis-GMA plus TEGDMA, was light-cured for 1 min on each side of the specimen. All specimens were formed in the molds covered with mylar strips clamped between glass slides. The TPH specimens were demolded after curing; the other specimens were incubated in a 100% humidity humidior at 37°C for 24 h before being demolded. All the flexural specimens were then immersed in distilled water at 37°C for 24 h before being fractured.

2.3. Mechanical properties, fluoride release, and polishability

The flexural specimens were immersed in distilled water at 37°C for 24 h prior to testing. A standard three-point flexural test [43] with a span of 10 mm was used to fracture the specimens at a crosshead speed of 0.5 mm/min on a computer-controlled Universal Testing Machine (model 5500R, Instron Corp., MA). The following properties were determined: flexural strength, modulus, and work-of-fracture (the energy required to fracture the specimen, obtained from the area under the load-displacement curve divided by the specimen's cross-sectional area).

Fluoride release was measured after storage periods of 1, 7, 14, 30, 60 and 90 days. To minimize dehydration and surface cracking [31], the glass ionomer specimens were immersed in distilled water within 1 h after they were taken out of the humidior and demolded. Four specimens were tested for each material. Each specimen was immersed in 2.5 ml water in a capped polystyrene tube (Falcon 2054, Becton Dickinson, NJ) and stored in a 37°C oven. After each prescribed storage period, 1 ml of the storage solution was collected from each tube; 1 ml of fresh deionized water was then added to the tube for further storage. 1 ml of a buffer solution (TISAB II, Orion Research, Inc., Boston, MA) was added to the collected solution for fluoride concentration measurement. A fluoride ion-selective electrode (model 94-09, Orion Research, Inc., Boston, MA) was used to measure the fluoride concentration in the solution while the solution was stirred with a poly(tetrafluoroethylene)-coated magnetic bar. An experimental curve of relative millivolts as a function of fluoride concentration was generated by use of various buffered dilutions of the standard solution (Orion Research, Inc., Boston, MA). Standard curves between approximately 0.04 and 10 ppm were used to generate calibration curves for the electrode. The amount of fluoride measured was converted into micrograms of F^- released per unit specimen area ($\mu\text{g}/\text{cm}^2$) according to previous methods [44]. The cumulative amount of fluoride

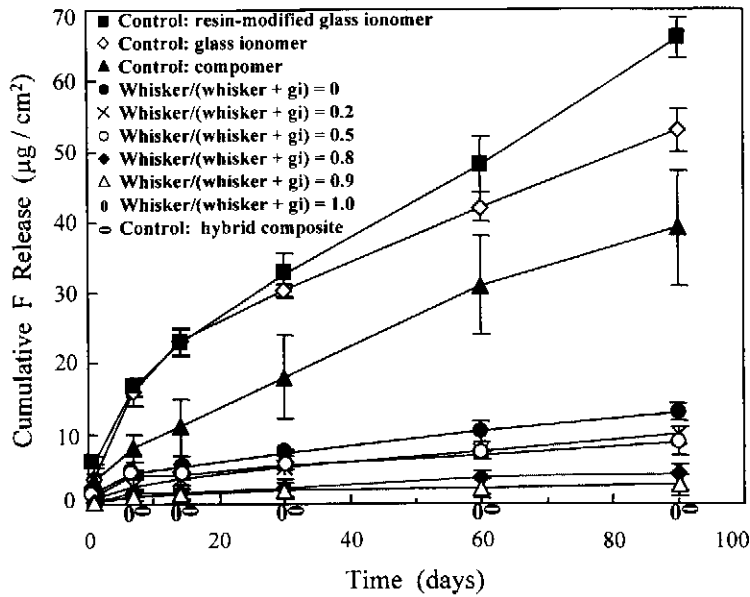


Fig. 2. Cumulative fluoride release as a function of days stored in distilled water at 37°C. "gi" designates precurd glass ionomer particles.

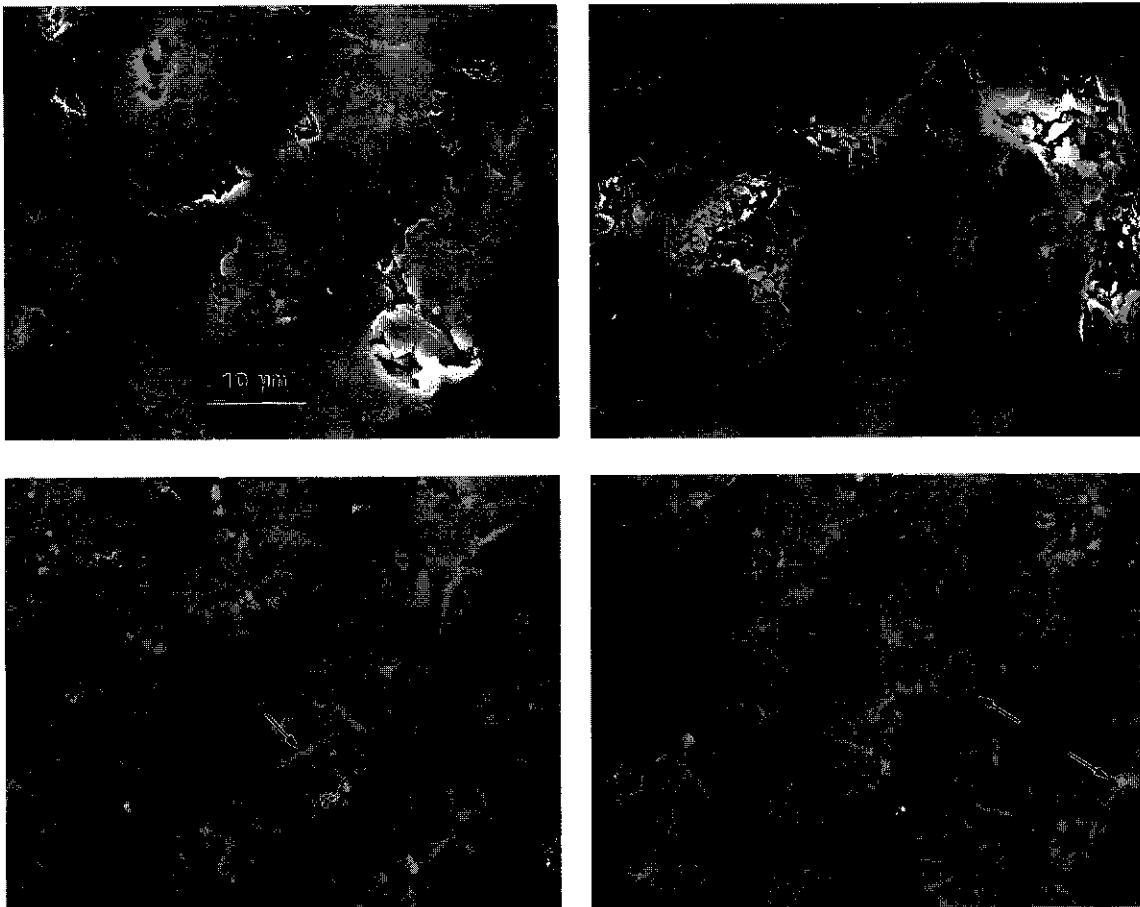


Fig. 3. SEM of polished surfaces of: (A) glass ionomer (Ketac); (B) resin-modified glass ionomer (Vitremer); and (C) and (D) whisker composites at whisker/(whisker + precurd glass ionomer) ratios of 0.91 and 0.5, respectively. "w" designates whiskers, "gi" designates precurd glass ionomer particles. Pores and microcracks were found in glass ionomer and resin-modified glass ionomer. The whisker composites had smoother surfaces, with individual whiskers and precurd glass ionomer particles well dispersed in the resin matrix. The same magnification was used for (A)–(D).

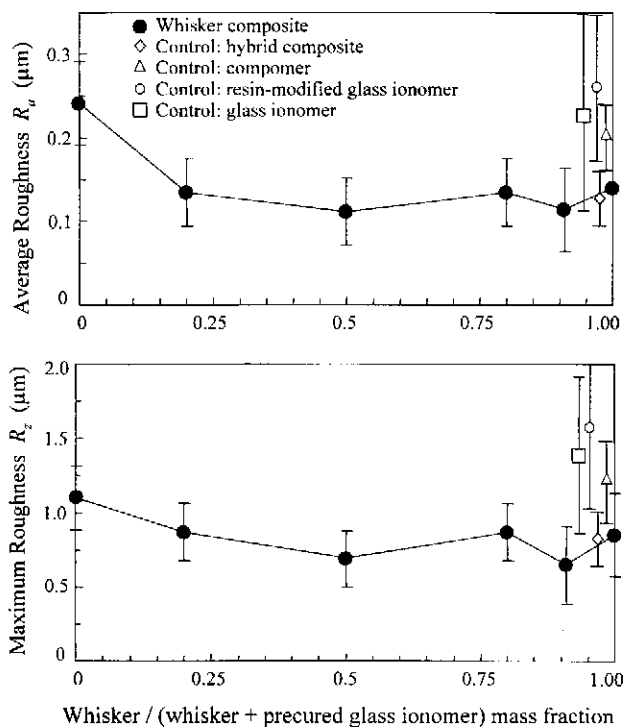


Fig. 4. Average and maximum roughness values (mean (SD); $n = 6$) of clinically polished surfaces measured by profilometry as a function of $w/(w + gi)$. Values of the four control materials are plotted near the right axis for comparison.

release was then calculated after each storage period [34,45].

Six specimens of $2 \times 2 \times 8$ mm dimensions of each material were finished on one side simulating clinical conditions using a 12-fluted carbide bur followed by a 30-fluted bur, and polished with a rubber polishing tip. The average surface roughness (R_a) and maximum roughness (R_z) of the polished surfaces were measured using a computer-controlled profilometry system (Perthometer Concept, Mahr Corp., Cincinnati, OH). The debris produced during polishing of the composites with 12-fluted carbide bur was collected and placed onto a scanning electron microscopy (SEM) stub, sputter-coated with gold, and examined with a SEM (model JSM-5300, JEOL, Inc., Peabody, MA).

One-way ANOVA and Kruskal–Wallis Analysis of Variance on Ranks were performed to detect significant ($\alpha = 0.05$) effects of filler fraction on mechanical properties and polishability. Tukey's and Dunn's multiple comparison tests were used at a family confidence coefficient of 0.95 to group and rank the measured values.

3. Results

Mechanical properties as a function of whisker/(whisker+precured glass ionomer) mass fraction, or $w/(w+gi)$, are shown in Fig. 1. Values of the four controls

are shown by open symbols at the right axis. Flexural strength showed a relatively steep increase with increasing $w/(w + gi)$. The flexural strength (mean (SD); $n = 6$) at $w/(w+gi) = 0.0$ was (43 (6)) MPa. It increased to (152 (15)) MPa at $w/(w+gi) = 0.91$, and (196 (10)) MPa at $w/(w+gi) = 1.0$, which were significantly higher than those of the controls (Tukey's multiple comparison test; family confidence coefficient = 0.95). Flexural modulus of whisker composite increased from (3.9 (0.2)) GPa at $w/(w+gi) = 0.0$ to (7.6 (0.4)) GPa at $w/(w + gi) = 0.5$, and then plateaued. Work-of-fracture of whisker composite was (0.3 (0.1)) kJ/m^2 at $w/(w + gi) = 0.0$; it increased to (3.9 (0.7)) kJ/m^2 at $w/(w+gi) = 1.0$, which was significantly higher than those of the controls.

Cumulative fluoride release results are plotted in Fig. 2. "gi" designates "precured glass ionomer particles". Fluoride release for the control hybrid composite and the whisker composite at $w/(w+gi) = 1.0$ was not detectable. Fluoride release for the whisker composites was lower than the fluoride release of the control materials, with the greatest release at $w/(w+gi) = 0.2$ being nearly 20% that of the glass ionomer control.

SEM micrographs of the surfaces polished under simulated clinical procedures are shown in Fig. 3 for: (A) glass ionomer; (B) resin-modified glass ionomer; (C) whisker composite at $w/(w+gi) = 0.91$; and (D) whisker composite at $w/(w+gi) = 0.5$. Pores and microcracks were frequently found in the polished surfaces of glass ionomer and resin-modified glass ionomer (Fig. 3A and B). The whisker composites had more continuous surfaces, with examples shown in Fig. 3C and D, where "w" designates whiskers, and "gi" designates precured glass ionomer particles. The whiskers and precured glass ionomer particles ("gi" in Fig. 3D) appeared to be well dispersed in and bonded to the resin matrix. SEM observations of the polished surfaces of whisker composites revealed smooth surfaces with little porosity. These observations are supported by the results of profilometric measurements in Fig. 4. Although the roughness values (mean (SD); $n = 6$) of the resin-modified glass ionomer and the glass ionomer are not significantly different from those of the other composites (Dunn's multiple comparison method; family confidence coefficient = 0.95), the resin-modified glass ionomer and the glass ionomer tend to have rougher surfaces. The roughness values of the whisker composites and the hybrid composite control are nearly the same.

SEM micrographs of polishing debris are shown in Fig. 5 for: (A) glass ionomer; (B) whisker composite at $w/w+gi = 0.5$; (C) whisker composite at $w/w+gi = 0.91$; and (D) an area of C at a higher magnification. The polishing chips or smeared sheets (big arrows), and the fine particles (small arrows) produced during polishing of the whisker composites are similar to those of glass ionomer. Intact whiskers were rarely found in the polishing debris when examined in the SEM. At a higher magnification, whisker fragments (Fig. 5D) were occasionally found in

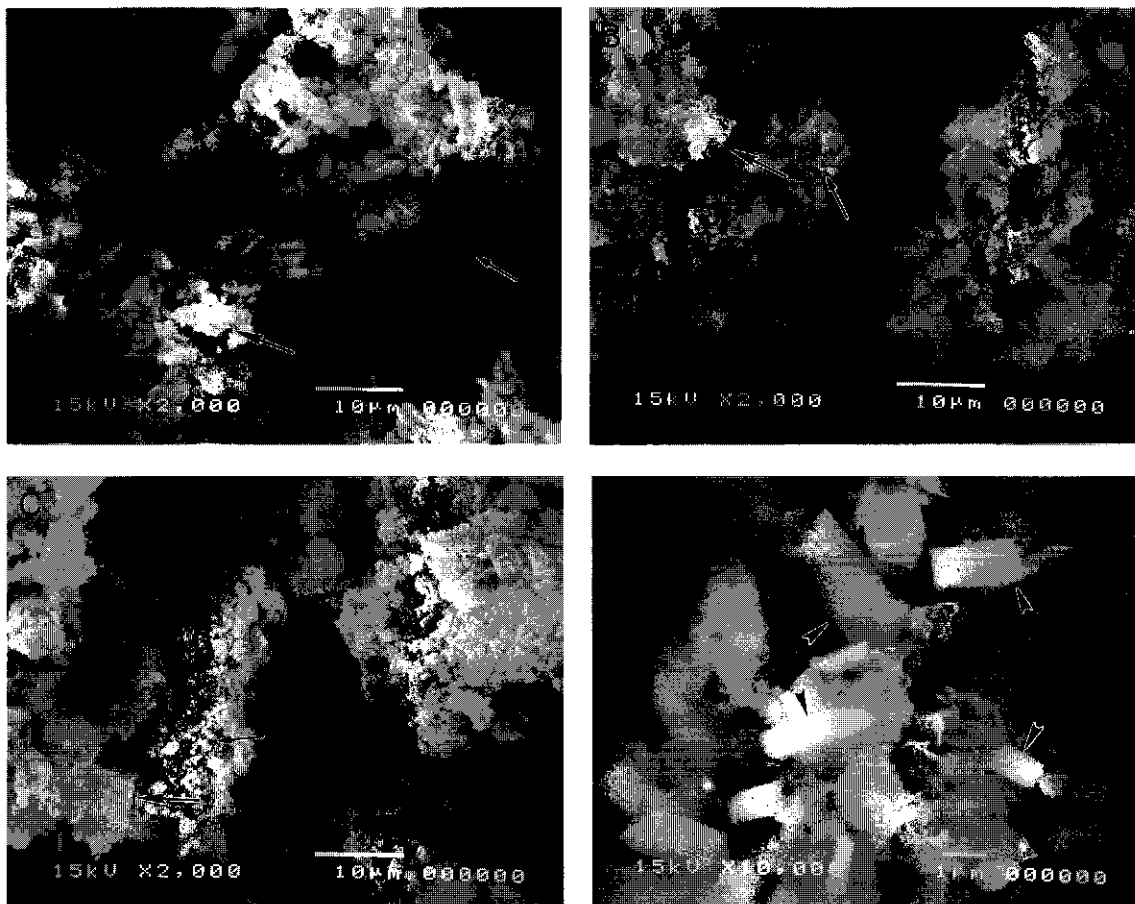


Fig. 5. SEM of polishing debris for: (A) glass ionomer control; (B) and (C) whisker composites at $w/(w + gi)$ of 0.5 and 0.91, respectively; and (D) an area of C at a higher magnification. The polishing chips or smeared sheets (big arrows) and fine particles (small arrows) are similar for all the materials. Whiskers were not found in most of the polishing debris except in a few areas, an example of which is shown in (D). The whiskers in the polishing debris had a length to diameter ratio of approximately 2–4.

the polishing debris and they had an aspect ratio (length-to-diameter ratio) ranging from approximately 2–4.

4. Discussion

In the results of the present study it was found that ceramic whisker reinforcement can be combined with a fluoride-releasing filler to yield composites with substantially improved mechanical properties and a moderate level of fluoride release. The flexural strength values of the control hybrid composite, glass ionomer, and resin-modified glass ionomer, measured in the present study, were in the range of those reported in previous studies on similar materials [28,31,39,48]. The fusing of silica glass particles onto the surface of individual whiskers has facilitated whisker silanization and improved the whisker retention in the matrix by providing rougher whisker surfaces [13]. Silica particles appeared to be well bonded to the whiskers due to high temperature fusion, resulting in a significant improvement in composite mechanical properties [13]. The high strength of the single crystal whiskers [17] contributes to the compo-

site strength; the composite strength was proportional to the strength of fibers or whiskers [18]. The elongated shapes of the whiskers also contribute to the reinforcement efficacy, as elongated fillers are more effective in bridging and resisting cracks than round-shaped fillers [46], with enamel rods in natural teeth being one example [47]. The small size of whiskers contributes to the polishability of the composites. Previous studies had used glass fibers of a diameter of approximately $10\ \mu\text{m}$ and a length of a few hundred μm to reinforce dental composites [3,9]. The size of the whiskers used in the present study were orders of magnitude smaller than most glass fibers and other ceramic fibers [15,19]. These small whiskers not only allowed a relatively uniform distribution in the matrix, but also yielded composites with roughness of polished surfaces similar to that of a small-particle hybrid resin composite control.

Free fibers and whiskers of less than $1\ \mu\text{m}$ in diameter and more than $10\ \mu\text{m}$ in length may present a potential inhalation and carcinogenic hazard [49–51]. SEM examination of the collected polishing debris of the whisker composites revealed chips, smeared sheets, and fine particles similar to those of the control materials. Only occasionally

were short whisker fragments found in the polishing debris from the whisker composites (Fig. 5D), and the fragment lengths were much shorter than either the as-received whiskers or the whiskers observed in the surfaces of cured composites (Fig. 3D). The much shorter whisker fragments found in the polishing debris were likely a result of whisker fracture during polishing. Previous studies demonstrated that elongated silicon nitride whiskers fractured into fine powders during machining or grinding [16]. That whiskers were fractured rather than dislodged from the matrix during polishing is consistent with the observation that polished whisker composites were free of pores or holes from whisker dislodgment (Fig. 3). Free whiskers less than 0.5 μm in diameter and more than 10 μm in length were not found in the polishing of the present study, consistent with the polishing and machining of other whisker composites [16]. Further studies are needed to investigate the clinical effects of the polishing debris of whisker composites.

To conclude, a novel filler system of silica-fused ceramic whiskers mixed with precured glass ionomer particles significantly improved the mechanical properties of resin composites formulated to release fluoride. Flexural strength, modulus and work-of-fracture (an indication of toughness) of the composites increased with increasing $w/(w + gi)$ ratio. On the other hand, the cumulative fluoride release of the composite increased when the $w/(w + gi)$ ratio was decreased. The elongate-shaped, high strength single crystal whiskers contributed to the strengthening and toughening of the composite, while the precured glass ionomer filler contributed to the fluoride release. The small size of whiskers enhanced the polishability of the composites, yielding polished surfaces comparable to that of a hybrid resin composite control. Further studies should investigate the wear behavior and long term water-aging response of these ceramic single crystal whisker-reinforced, fluoride-releasing resin composites.

Disclaimer: Certain commercial materials and equipment are identified in this paper to specify experimental procedures. In no instance does such identification imply recommendation by NIST or the ADA Health Foundation or that the material identified is necessarily the best available for the purpose.

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References

- [1] Bowen RL, Eichmiller FC, Marjenhoff WA. Glass-ceramic inserts anticipated for megafilled composite restorations. *J Am Dent Assoc* 1992;122:71–5.
- [2] Ferracane JL, Marker VA. Solvent degradation and reduced fracture toughness in aged composites. *J Dent Res* 1992;71:13–9.
- [3] Willems G, Lambrechts P, Braem M, Cclis 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] Sakaguchi RL, Versluis A, Douglas WH. Analysis of strain gage method for measurement of post-gel shrinkage in resin composites. *Dent Mater* 1997;13:233–9.
- [6] 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.
- [7] Eick JD, Kaufman GM, Chappelow CC. Applications of polymers: what are the future trends? *Acad Dent Mater Trans* 1997;10:89–98.
- [8] Condon JR, Ferracane JL. In vitro wear of composite with varied cure, filler level, and filler treatment. *J Dent Res* 1997;76:1405–11.
- [9] Krause WR, Park SH, Straup RA. Mechanical properties of Bis-GMA resin short glass fiber composites. *J Biomed Mater Res* 1989;23:1195–211.
- [10] Bayne SC, Thompson JY. Mechanical property analysis of two admixed PRIMM-modified commercial dental composites. *Acad Dent Mater Trans* 1996;9:238.
- [11] Bayne SC, Heymann HO, Swift Jr ED. Update on dental composite restorations. *J Am Dent Assoc* 1994;125:687–701.
- [12] Wilder Jr. AD, Bayne SC, Heymann HO. Long-term clinical performance of direct posterior composites. *Acad Dent Mater Trans* 1996;9:151–69.
- [13] Xu HHK, Martin TA, Antonucci JM, Eichmiller FC. Ceramic whisker reinforcement of dental resin composites. *J Dent Res* 1999;78:706–12.
- [14] Xu HHK, Eichmiller FC. Reinforcement of dental and other composite materials. US Patent No. 5,861,445, January 1999.
- [15] Lawn BR. Fracture of brittle solids. London: Cambridge University Press, 1993 (chap. 8).
- [16] Xu HHK, Jahanmir S, Ives LK. Material removal and damage formation mechanisms in grinding silicon nitride. *J Mater Res* 1996;11:1717–24.
- [17] Iwanaga H, Kawai C. Tensile strength of silicon nitride whiskers synthesized by reacting amorphous silicon nitride and titanium dioxide. *J Am Ceram Soc* 1998;81:773–6.
- [18] Xu HHK. Crack-bridging toughening of continuous-fiber ceramic composites at ambient and elevated temperatures. PhD thesis, University of Maryland at College Park, 1993.
- [19] 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.
- [20] MacInnis WA, Ismail A, Brogan H. Placement and replacement of restorations in a military population. *Can Dent Assoc J* 1991;57:227–31.
- [21] Wesenberg G, Hals E. The structure of experimental in vitro lesions around glass ionomer cement restorations in human teeth. *J Oral Rehabil* 1980;7:175–84.
- [22] Palenik CJ, Behnen MJ, Setcos JC, Miller CH. Inhibition of microbial adherence and growth by various glass ionomers in vitro. *Dent Mater* 1992;8:16–20.
- [23] Leinfelder KF. Glass ionomers: current clinical developments. *J Am Dent Assoc* 1993;124:62–4.
- [24] Benelli EM, Serra MC, Rodrigues Jr. AL, Cury JA. In situ anticariogenic potential of glass ionomer cement. *Caries Res* 1993;27:280–4.
- [25] Souto M, Donly KJ. Caries inhibition of glass ionomers. *Am J Dent* 1994;7:122–4.
- [26] Hsu CYS, Donly KJ, Drake DR, Wefel JS. Effects of aged fluoride-containing restorative materials on recurrent root caries. *J Dent Res* 1998;77:418–25.

- [27] Wilson AD, Kent BE. A new translucent cement for dentistry—the glass ionomer cement. *Br Dent J* 1972;132:133–5.
- [28] Prosser HJ, Powis DR, Wilson AD. Glass-ionomer cements of improved flexural strength. *J Dent Res* 1986;65:146–8.
- [29] McLean JW. Cermets cements. *J Am Dent Assoc* 1990;120:43–7.
- [30] Antonucci JM, McKinney JE, Stansbury JW. Resin-modified glass-ionomer dental cements. US Patent Application No. 7160856, 1988.
- [31] Mathis RS, Ferracane JL. Properties of a glass-ionomer/resin-composite hybrid material. *Dent Mater* 1989;5:355–8.
- [32] Mitra SB. Photocurable ionomer cement systems. Eur Patent Application No. 88312127, publication No. 0323120, 1989.
- [33] Swartz ML, Phillips RW, Clark HE. Long-term F release from glass ionomer cements. *J Dent Res* 1984;63:158–60.
- [34] Mitra SB. In vitro fluoride release from a light-cured glass-ionomer liner/base. *J Dent Res* 1991;70:75–8.
- [35] Hicks MJ, Flaitz CM. Caries-like lesion formation around fluoride-releasing sealant and glass ionomer. *Am J Dent* 1992;5:329–34.
- [36] Diaz-Arnold AM, Holmes DC, Wistrom DW, Swift Jr. EJ. Short-term fluoride release/uptake of glass ionomer restoratives. *Dent Mater* 1995;11:96–101.
- [37] Lloyd CH, Butchart DGM. The retention of core composites, glass-ionomers and cermets by a self-threading dentin pin: the influence of fracture toughness upon failure. *Dent Mater* 1990;6:185–8.
- [38] Nicholson JW, Anstice HM, McLean JW. A preliminary report on the effect of storage in water on the properties of commercial light-cured glass ionomer cement. *Br Dent J* 1992;173:98–101.
- [39] Mitra SB, Kedrowski BL. Long-term mechanical properties of glass ionomers. *Dent Mater* 1994;10:78–82.
- [40] Kao EC, Culbertson BM, Xie D. Preparation of glass ionomer cement using *N*-acryloyl-substituted amino acid monomers—evaluation of physical properties. *Dent Mater* 1996;12:44–51.
- [41] Sidhu SK, Sherriff M, Watson TF. The effects of maturity and dehydration shrinkage on resin-modified glass ionomer restorations. *J Dent Res* 1997;76:1495–501.
- [42] Wilson AD, McLean JW. Glass ionomer cement. Chicago: Quintessence, 1988 (chap. 1).
- [43] American Society for Testing and Materials. ASTM F417-78: Standard test method for flexural strength of electrical grade ceramics. Philadelphia, PA: ASTM, 1984.
- [44] Fukazawa M, Matsuya S, Yamane M. The mechanism for erosion of glass-ionomer cements in organic acid buffer solutions. *J Dent Res* 1990;69:1175–9.
- [45] Verbeeck RMH, De Moor RJG, Van Even DFJ, Martens LC. The short-term fluoride release of a hand-mixed vs. capsulated system of a restorative glass-ionomer cement. *J Dent Res* 1993;72:577–81.
- [46] Xu HHK, Jahanmir S. Effect of microstructure on damage tolerance in grinding dental glass ceramics. *J Mater Res* 1998;13:2231–6.
- [47] 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.
- [48] Ferracane JL, Mitchem JC. Properties of posterior composites: results of round robin testing for a specification. *Dent Mater* 1994;10:92–9.
- [49] Stanton MF, Layard M, Tegeris A, Miller E, May M, Morgan E, Smith A. Relation of particle dimension to carcinogenicity in amphibole asbestos and other fibrous minerals. *J Nat Cancer Inst* 1981;67:965–75.
- [50] Birchall JD, Stanley DR, Mockford MJ, Pigott GH, Pinto PJ. Toxicity of silicon carbide whiskers. *J Mater Sci Lett* 1988;7:350–2.
- [51] Mossman BT, Bignon J, Corn M, Seaton A, Gee JBL. Asbestos: scientific developments and implications for public policy. *Science* 1990;247:294–301.