

Single-Crystalline Ceramic Whisker-Reinforced Carboxylic Acid-Resin Composites with Fluoride Release

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Clinical Relevance

Carboxylic acid-resin composites containing ceramic whiskers and fluorosilicate glass release fluoride and possess flexural strength and work-of-fracture substantially higher than those of a traditional glass ionomer, a resin-modified glass ionomer, or a compomer.

SUMMARY

Currently available glass-ionomer, resin-modified glass-ionomer, and compomer materials have relatively low strength and toughness and, therefore, are inadequate for use in large stress-bearing posterior restorations. In the present study, ceramic single-crystalline whiskers were mixed with fluorosilicate glass particles and used as fillers to reinforce experimental carboxylic acid-resin composites. The carboxylic acid was a monofunctional methacryloxyethyl phthalate (MEP). Five mass fractions of whisker/(whisker + fluorosilicate glass), and corresponding resin (resin + MEP), were evaluated. Four control materials were also tested for comparison: a glass ionomer, a resin-modified glass ionomer, a com-

omer, and a hybrid composite resin. Flexural specimens were fabricated to measure the flexural strength, elastic modulus, and work-of-fracture (an indication of toughness). Fluoride release was measured by using a fluoride ion selective electrode. The properties of whisker composites depended on the whisker/(whisker + fluorosilicate glass) mass fraction. At a mass fraction of 0.8, the whisker composite had a flexural strength in MPa (mean \pm sd; $n = 6$) of 150 ± 16 , significantly higher than that of a glass ionomer (15 ± 7) or a compomer control (89 ± 18) (Tukey's multiple comparison test; family confidence coefficient = 0.95). Depending on the ratio of whisker:fluorosilicate glass, the whisker composites had a cumulative fluoride release up to 60% of that of a traditional glass ionomer. To conclude, combining ceramic whiskers and fluorosilicate glass in a carboxylic acid-resin matrix can result in fluoride-releasing composites with significantly improved mechanical properties.

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INTRODUCTION

It had been reported that approximately half of all restorative dentistry involved the replacement of existing restorations, and about 40% of all replacements were attributed to recurrent caries (MacInnis, Ismail & Brogan, 1991). There is strong evidence that the sustained release of small amounts of fluoride could be a

substantial benefit for a dental restoration because the fluoride could enrich neighboring enamel or dentin to combat secondary caries (Wesenberg & Hals, 1980; Palenik & others, 1992; Leinfelder, 1993; Benelli & others, 1993; Souto & Donly, 1994; Hsu & others, 1998). Glass ionomer (Wilson & Kent, 1972; Prosser, Powis & Wilson, 1986; McLean, 1990) and resin-modified glass-ionomer materials (Mathis & Ferracane, 1989; Mitra, 1989) have received much attention due to their significant release of fluoride, the uptake of fluoride into cavity walls and plaque, and the enhanced reprecipitation of calcium and phosphate promoted by the fluoride release (Wesenberg & Hals, 1980; Swartz, Phillips & Clark, 1984; Swift, 1989a, b; Mitra, 1991; Hicks & Flaitz, 1992; Benelli & others, 1993; Díaz-Arnold & others, 1995). The inferior mechanical properties of glass-ionomer and resin-modified glass-ionomer materials, however, have limited their use (Prosser & others, 1986; Lloyd & Butchart, 1990; Nicholson, Anstice & McLean, 1992; Mitra & Kedrowski, 1994; Kao, Culbertson & Xie, 1996). It was predicted that "the most intractable problem is likely to be lack of strength and toughness" (Wilson & McLean, 1988). The addition of a resin in the matrix did not significantly reduce the problems of glass-ionomer materials (Sidhu, Sherriff & Watson, 1997).

Recently, a novel method of ceramic whisker reinforcement was developed that resulted in dental composite resins with substantially increased strength and toughness (Xu & others, 1999a). Currently available composite resins, although significantly improved (Willems & others, 1992; Anusavice, 1996; Bayne & Thompson, 1996; Ferracane & others, 1997; Eick, Kaufman & Chappelow, 1997; Loza-Herrero & others, 1998), are still inadequate for use as large stress-bearing posterior restorations involving cusps (Wilder, Bayne & Heymann, 1996; Anusavice, 1996). In the ceramic whisker reinforcement method (Xu & others, 1999a), silica glass particles were fused onto high-strength, fine-sized ceramic single-crystalline whiskers at high temperatures. These whiskers were then silanized and incorporated into dental resins. A nearly twofold increase was achieved in the flexural strength and fracture toughness of this improved composite resin. In addition, the composite's resistance to contact damage and microcracking was also improved. The whisker composite restoration had a whitish color and a surface roughness after clinical polishing similar to that of a conventional composite resin filled with fine glass particles (Xu & others, 1999b). However, these studies did not investigate the ceramic whisker reinforcement of dental restorative materials that release fluoride.

The aim of the present study was to investigate the ceramic whisker reinforcement of dental restorative materials with fluoride release. Fluorosilicate glass particles were mixed with ceramic whiskers and used as

a filler for a dental resin containing a carboxylic acid monomer. Five whisker/(whisker + fluorosilicate glass) mass fractions of 0.5, 0.7, 0.8, 0.9, and 1.0 were evaluated. The resin/(resin + carboxylic acid monomer) mass fraction was equal to the whisker/(whisker + fluorosilicate glass) mass fraction for each composite. The whisker composites were tested for flexural strength, elastic modulus, work-of-fracture, and fluoride release. Four control materials representative of acceptable clinical performance and different levels of fluoride release were also tested: a traditional glass ionomer, a resin-modified glass ionomer, a compomer, and a hybrid composite resin.

METHODS AND MATERIALS

Filler Powder Preparation

Ceramic silicon nitride single-crystalline (β -Si₃N₄) whiskers (UBE Industries, Ltd, Tokyo, Japan) with diameters ranging from 0.1 μ m to 1.5 μ m (mean = 0.4 μ m) and lengths ranging from 2 μ m to 20 μ m (mean = 5 μ m) were mixed with fumed silica having a nominal particle size of 0.04 μ m (Aerosil OX50; Degussa Corp, South Plainfield, NJ 07080). 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 vacuum until dry. The silica particles were fused onto the surfaces of whiskers to facilitate silanization and to roughen the whisker surface for enhanced retention in the matrix. To fuse the silica particles onto the whiskers, the dried mixture was heated in air for 30 minutes at a temperature of 800°C. The heat-treated powder was silanized by mixing it with 0.04 mass fraction of 3-methacryloxypropyltrimethoxysilane (MPTMS) and 0.02 mass fraction of n-propylamine in cyclohexane using a rotary evaporator in a 90°C water bath until dry (Xu & others, 1999a).

The silanized whiskers were manually mixed by use of spatulation with an ion-leachable fluorosilicate glass (strontium aluminofluorosilicate; Caulk/Dentsply, Inc, Milford, DE 19963) of particles with sizes ranging approximately from 0.5 μ m to 10 μ m with a mean of about 2 μ m. The fluorosilicate particles were deliberately not silanized to promote their reaction with the carboxylic acid monomer of the resin system and allow for maximum fluoride release. The following whisker:fluorosilicate glass mass ratios were evaluated: 1:1, 7:3, 8:2, 9:1, and 1:0. These ratios corresponded to a whisker/(whisker + fluorosilicate) mass fraction of 0.5, 0.7, 0.8, 0.9, and 1.0, respectively. Whisker mass fractions less than 0.5 were not tested, as the amount of whiskers may not be sufficient for substantial improvement in the composite mechanical properties.

Resin-Carboxylic Acid Monomer Preparation

Modification of a two-part, chemically-activated resin was used to prepare the experimental carboxylic acid-

resin systems. Part I, the initiator resin, consisted of monomers in mass fractions of 0.48975 BIS-GMA (bisphenol glycidyl methacrylate) and 0.48975 TEGDMA (triethylene glycol dimethacrylate), with 0.0005 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 0.02 benzoyl peroxide (BPO). Part II, the accelerator resin, consisted of mass fractions of 0.495 BIS-GMA and 0.495 TEGDMA, with 0.01 *N,N*-dihydroxyethyl-*p*-toluidine (DHEPT) as the polymerization accelerator. A monofunctional carboxylic acid monomer (methacryloxyethyl phthalate, or MEP) (Lot 430-49; Esschem Inc, Linwood, PA 19061) was added to each of the resins to form MEP-resin two-part systems. No additional BPO or DHEPT was added to the resins. Five MEP-resin systems were made with the following resin/(resin + MEP) mass fractions: 0.5, 0.7, 0.8, 0.9, and 1.0.

Paste Preparation and Specimen Fabrication

The five different resin/(resin + MEP) mass fractions were designed to be the same as the five whisker/(whisker + fluorosilicate glass) mass fractions. In mixing the filler powder with the MEP-resin liquid to form a paste, the mass fraction of whisker/(whisker + fluorosilicate glass) was equal to that of resin/(resin + MEP). For example, the liquid with a resin/(resin + MEP) mass fraction of 0.5 was only mixed with the filler powder with a whisker/(whisker + fluorosilicate glass) mass fraction of 0.5. For each mass fraction, two pastes were mixed manually by use of spatulation: the initiator MEP-resin and whisker-fluorosilicate paste, and the accelerator MEP-resin and whisker-fluorosilicate paste. A filler level of a mass fraction of 55% was used for each paste (Xu & others, 1999a). Equal masses of the two pastes were then mixed by spatulation, filled into a mold and hardened in approximately two minutes to make a specimen. The flexural specimens had dimensions of approximately 2 mm x 2 mm x 20 mm. The specimens for fluoride release testing had dimensions of approximately 2 mm x 2 mm x 8 mm. Each specimen was incubated at 37°C for 15 minutes to cure chemically, and then demolded. A total of 60 flexural specimens were made for the whisker composites, with 12 specimens at each whisker/(whisker + fluorosilicate glass) mass fraction. A total of 20 fluoride release specimens were made with four specimens at each whisker/(whisker + fluorosilicate glass) mass fraction.

Specimens of four control materials were also fabricated to provide representative reference for mechanical properties and fluoride release. The first control was a traditional glass ionomer (Ketac-Bond; ESPE, Seefeld, Germany). The manufacturer has recommended a powder:liquid weight ratio of 3.4:1 for bonding applications and a higher ratio of 4-5:1 for crown post build-ups. In the present study, a powder:liquid weight ratio of 5:1 was used and the paste was filled into steel

molds and hardened to make specimens. A resin-modified glass ionomer (Vitremar; 3M Dental Products, St Paul, MN 55144) was mixed to form a paste according to the manufacturer's instructions, filled into the mold, and light cured (Triad 2000; Dentsply International, Inc, York, PA 17405) for one minute on each side of the specimen. A compomer (Dyract; Caulk/Dentsply) was filled into the mold and light cured for one minute on each side of the specimen. Specimens of the traditional glass ionomer, the resin-modified glass ionomer, and the compomer were kept in the molds covered with Mylar strips plus glass slides that then were mechanically clamped. They were incubated in a humidior to minimize dehydration at 37°C for 24 hours and then demolded and tested as described below. A hybrid composite resin (TPH; Caulk/Dentsply), consisting of silicate and barium glass particles of about 0.8 μm in diameter and a filler level of 78% mass fraction in a matrix resin of TEGDMA plus a urethane-modified BIS-GMA, was light cured for one minute on each side of the specimen. The TPH specimens were incubated at 37°C for 24 hours and then demolded. The dimensions of the control specimens were the same as those of the whisker composite specimens. A total of 48 flexural specimens were made with 12 specimens for each control material. A total of 16 fluoride release specimens were made with four specimens for each control material.

Mechanical Testing and Fluoride Release Measurement

The flexural specimens were treated in two groups to evaluate the effect of water immersion on composite properties. Each group had 54 specimens with six specimens for each of the nine materials: five whisker composites and four control materials. For the first group, the flexural specimens were incubated and demolded as described above. They were then, without any immersion in water, fractured in a flexural test. The glass-ionomer and resin-modified glass-ionomer specimens were fractured within one hour after being taken out of the humidior to minimize dehydration. For the second group, the flexural specimens were demolded and additionally immersed in distilled water at 37°C for 24 hours prior to the flexural test.

A standard three-point flexural test (American Society for Testing and Materials, 1984) with a span of 10 mm was used to fracture the specimens at a crosshead speed of 0.5 mm per minute on a computer-controlled Universal Testing Machine (model 5500R; Instron Corp, Canton, MA 02021). The following properties were evaluated: flexural strength, elastic modulus, and work-of-fracture (the energy required to fracture the specimen obtained from the area under the load-displacement curve normalized 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 (Mathis & Ferracane, 1989), the glass-ionomer specimens were immersed in distilled water within one hour after they were taken out of the humidifier and demolded. Four bar specimens were tested for each material. Each bar was immersed in 2.5 mL water in a capped polystyrene tube (Falcon 2054; Becton Dickinson, Franklin Lakes, NJ 07417) stored in a 37°C oven. Preliminary studies indicated that 2.5 mL of water was sufficient for one Ketac specimen to avoid fluoride saturation of the solution. The amount of fluoride release of some of the whisker composites with high whisker contents was relatively low, and a large amount of storage water (eg, 10 mL) resulted in a low fluoride concentration and hence lower measurement accuracy. After each prescribed storage period, 1 mL of the storage solution was collected from each tube; 1 mL fresh deionized water was then added to the tube for further storage. A buffer solution of 1 mL (TISAB II; Orion Research, Inc, Boston MA 02129) was added to the collected solution for fluoride concentration measurement. A fluoride selective electrode (model 94-09; Orion Research, Inc) was used to measure the fluoride concentration in the solution while the solution was stirred with a poly(tetrafluoroethylene)-coated magnetic bar. Standard curves between approximately 0.04 ppm and 10 ppm were used to calibrate the electrode. 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). The amount of fluoride measured was converted

Table 1a: Mechanical Properties of Specimens Without Water Immersion (mean \pm SD; n=6)*

Whisker/[whisker + fluorosilicate glass] (mass fraction)	Flexural strength (MPa)	Elastic modulus (GPa)	Work-of-fracture (kJ/m ²)
0.5	121 \pm 2	7.2 \pm 0.2	1.2 \pm 0.1
0.7	154 \pm 11	8.2 \pm 0.4	1.8 \pm 0.3
0.8	159 \pm 14	8.0 \pm 0.7	2.1 \pm 0.4
0.9	178 \pm 16	7.6 \pm 0.9	3.5 \pm 0.4
1.0	195 \pm 8	7.1 \pm 0.5	3.9 \pm 0.5
control: traditional glass ionomer	54 \pm 6	12.2 \pm 1.6	0.16 \pm 0.03
control: resin-modified glass ionomer	60 \pm 6	5.8 \pm 0.7	0.4 \pm 0.1
control: compomer	120 \pm 9	6.5 \pm 0.7	1.5 \pm 0.3
control: hybrid composite resin	134 \pm 18	7.3 \pm 0.7	1.7 \pm 0.6

*Flexural strength is the highest at whisker/[whisker + fluorosilicate glass] of 1.0, followed by those at 0.9 and 0.8, and the lowest for glass ionomer and resin-modified glass ionomer (Tukey's multiple comparison test; family confidence coefficient = 0.95).

Table 1b: Mechanical Properties of Specimens After 24 h Immersion in Distilled Water at 37° C*

Whisker/[whisker + fluorosilicate glass] (mass fraction)	Flexural strength (MPa)	Elastic modulus (GPa)	Work-of-fracture (kJ/m ²)
0.5	121 \pm 5	5.4 \pm 0.9	1.8 \pm 0.2
0.7	140 \pm 6	6.1 \pm 0.2	2.2 \pm 0.3
0.8	150 \pm 16	7.4 \pm 0.3	2.1 \pm 0.5
0.9	180 \pm 12	6.8 \pm 0.9	3.3 \pm 0.2
1.0	196 \pm 10	7.2 \pm 0.4	4.0 \pm 0.7
control: traditional glass ionomer	15 \pm 7	5.1 \pm 2.4	0.04 \pm 0.02
control: resin-modified glass ionomer	39 \pm 6	5.3 \pm 0.2	0.2 \pm 0.1
control: compomer	89 \pm 18	6.1 \pm 0.3	1.8 \pm 0.3
control: hybrid composite resin	120 \pm 16	4.9 \pm 0.8	2.4 \pm 0.8

*Strength is the highest at whisker/[whisker + fluorosilicate glass] of 1.0 and 0.9 followed by those at 0.8 and 0.7, lower for hybrid composite and compomer, and the lowest for glass ionomer (Tukey's multiple comparison test; family confidence coefficient = 0.95).

into micrograms of F⁻ released per unit specimen area (μ g/cm²) according to previous methods (Fukazawa, Matsuya & Yamane, 1990). The cumulative amount of fluoride release was then calculated after each storage period (Mittra, 1991; Verbeek & others, 1993).

One-way ANOVA was performed to detect significance ($\alpha = 0.05$) in material properties. Tukey's multiple comparison test was used at a family confidence coefficient of 0.95 to group and rank the measured values.

RESULTS

Figure 1 shows the flexural strength of the four control materials and the whisker composites at whisker/[whisker + fluorosilicate glass] mass fractions of 0.5, 0.7, 0.8, 0.9, and 1.0. For each whisker composite, the

Table 2: Cumulative Fluoride Release per Specimen Area ($\mu\text{g}/\text{cm}^2$) (mean \pm SD; n = 4)*

Whisker/[whisker + fluorosilicate glass] (mass fraction)	1 day	7 days	14 days	30 days	60 days	90 days
0.5	1.6 \pm 0.6	3.5 \pm 0.1	5.6 \pm 0.4	12.0 \pm 2.6	25.4 \pm 1.0	33.0 \pm 1.9
0.7	0.4 \pm 0.1	1.1 \pm 0.1	1.6 \pm 0.2	2.2 \pm 0.4	5.6 \pm 0.9	11.1 \pm 0.8
0.8	2.3 \pm 0.7	3.5 \pm 1.0	3.7 \pm 1.0	3.9 \pm 1.1	5.0 \pm 1.0	7.1 \pm 0.4
0.9	0.7 \pm 0.1	0.9 \pm 0.1	1.0 \pm 0.1	1.1 \pm 0.1	1.3 \pm 0.3	1.5 \pm 0.1
control: traditional glass ionomer	3.7 \pm 1.8	16 \pm 1.7	23.1 \pm 2.3	30.1 \pm 1.3	42.3 \pm 1.9	53.0 \pm 3.4
control: resin-modified glass ionomer	5.7 \pm 1.2	16.4 \pm 1.2	22.9 \pm 1.6	32.5 \pm 2.5	47 \pm 3.6	65.5 \pm 2.8
control: compomer	3.3 \pm 1.6	8.0 \pm 2.1	11.1 \pm 4.2	18.0 \pm 5.0	31.3 \pm 7.0	39.0 \pm 7.5

*Resin-modified glass ionomer had the highest fluoride release followed by glass ionomer and compomer. Among whisker composites, fluoride release was the highest at whisker/[whisker + fluorosilicate glass] of 0.5 (Tukey's multiple comparison test; family confidence coefficient = 0.95). Fluoride release of at whisker/[whisker + fluorosilicate glass] of 1.0 and the composite resin control was not detectable.

mass fraction of resin/(resin + MEP) was equal to that of the whisker/(whisker + fluorosilicate glass). "W/(W + FS)" designates "whisker/(whisker + fluorosilicate glass) mass fraction." In each bar graph, the first bar shows the strength of the specimens without water immersion, and the second bar shows the strength of specimens fractured after 24 hours of immersion in water at 37°C. The two bars in each plot with a horizontal line show strength values that are not significantly different ($p > 0.1$; Student's t-test); the two bars in each plot without a horizontal line show values that are significantly different ($p < 0.05$; Student's t-test). The flexural strength of all the whisker composites, the compomer, and the composite resin control did not decrease significantly after the one day of immersion in water, while that of the glass ionomer and the resin-modified glass ionomer decreased significantly during the water immersion.

Tables 1A and 1B show flexural properties of specimens without water immersion and after one day of immersion, respectively. Each value is mean with one standard deviation of six measurements. In each column, values with six repeats were statistically compared (Tukey's multiple comparison test; family confidence coefficient = 0.95). The flexural strength of the whisker composite increased with increasing of the mass fraction of whisker/(whisker + fluorosilicate glass), both without water immersion and with one day of immersion. The flexural strength of the whisker composites at whisker/(whisker + fluorosilicate glass) mass fractions of 1.0 and 0.9 was the highest; those at whisker/(whisker + fluorosilicate glass) mass fractions of 0.8 and 0.7 and the control composite resin were statistically similar; and those of the resin-modified glass ionomer and the traditional glass ionomer were the lowest.

Without water immersion, the traditional glass ionomer had the highest elastic modulus, followed by the whisker composites and the posterior composite control, then by the compomer and the resin-modified glass ionomer. After one day of immersion in water, the modulus of the traditional glass ionomer and the whisker composites became generally similar to each other. The work-of-fracture was the highest for the whisker composites at whisker/(whisker + fluorosilicate glass) mass

fractions of 1.0 and 0.9, both without water immersion and with one day of immersion. The traditional glass ionomer and the resin-modified glass ionomer had the lowest work-of-fracture values.

Results of the cumulative fluoride-release measurements are listed in Table 2. Each value is the mean with one standard deviation of six measurements. In each column, values with four repeats were statistically compared (Tukey's multiple comparison test; family confidence coefficient = 0.95). The fluoride release of the control composite resin and the whisker composite at a whisker/(whisker + fluorosilicate glass) mass fraction of 1.0 were not detectable. The amount of fluoride release of the glass ionomer and the resin-modified glass ionomer were generally not significantly different. Fluoride release of the whisker composite at a whisker/(whisker + fluorosilicate glass) mass fraction of 0.5 and the compomer control were not significantly different. Figure 2 plots the amount of fluoride release versus storage time for these materials. "RMGI" designates the resin-modified glass ionomer, "GI" designates the glass ionomer, and "W/(W + FS)" designates "whisker/(whisker + fluorosilicate glass) mass fraction," while the mass fraction of resin/(resin + MEP) = whisker/(whisker + fluorosilicate glass).

DISCUSSION

Results of the present study suggest that ceramic whisker reinforcement can substantially improve the mechanical properties of direct restorative materials formulated to release fluoride. Fusing silica glass particles onto the surfaces of individual whiskers not only facilitates whisker silanization, but may have also improved the whisker retention in the matrix by providing rougher whisker surfaces. In addition, two other

factors may have contributed to the efficacy of composite reinforcement. The first factor is the high strength and toughness of the ceramic whiskers. The single-crystalline whiskers have few structural defects and hence tensile strength values as high as 50 GPa (Iwanaga & Kawai, 1998). In comparison, the strength of glass fibers is approximately 3 GPa and that of polished bulk glass is about 0.1 GPa (Lawn, 1993). The fracture toughness of crystalline ceramics (silicon nitride, alumina, zirconia, etc) ranges from about 2 to 6 MPa•m^{1/2}, while that of glass is only about 0.7 MPa•m^{1/2} (Lawn, 1993). It was observed that while a microcrack can easily cut through a glass filler, the ceramic whiskers are more resistant to fracture (Xu & others, 1999a). The second factor that may have contributed to the reinforcement efficacy is the highly elongated shapes of the whiskers (eg, a diameter of 0.4 μm and a length of 5 μm). Elongated fillers have been observed to be more effective than particulate fillers in bridging a microcrack resisting it from propagating (Lawn, 1993; Xu & others, 1998) and in resisting dislodgement from the matrix. The size of the whiskers are orders of magnitude smaller than most glass fibers and ceramic fibers (eg, a diameter of 10 μm to 100 μm and a length of 100 μm to 1 mm) (Lawn, 1993; Xu & others, 1994). These small whiskers allow a relatively uniform distribution in the matrix with an acceptable composite polishability (Xu & others, 1999b).

Combining ceramic single-crystalline whiskers with fluorosilicate glass in resins modified by the presence of a carboxylic acid monomer in the present study have yielded restorative composites with superior strength that are still able to release fluoride. Compared with the hybrid composite resin control, which did not have fluoride release, the whisker-fluorosilicate composites not only released fluoride, but also had flexural strength values 60 MPa and 30 MPa higher, at whisker/(whisker + fluorosilicate glass) mass fractions of 0.9 and 0.8, respectively. The flexural strength values of the composite resin control, the glass ionomer, and the resin-modified glass ionomer measured in the present study were in the range of those reported in previous studies on

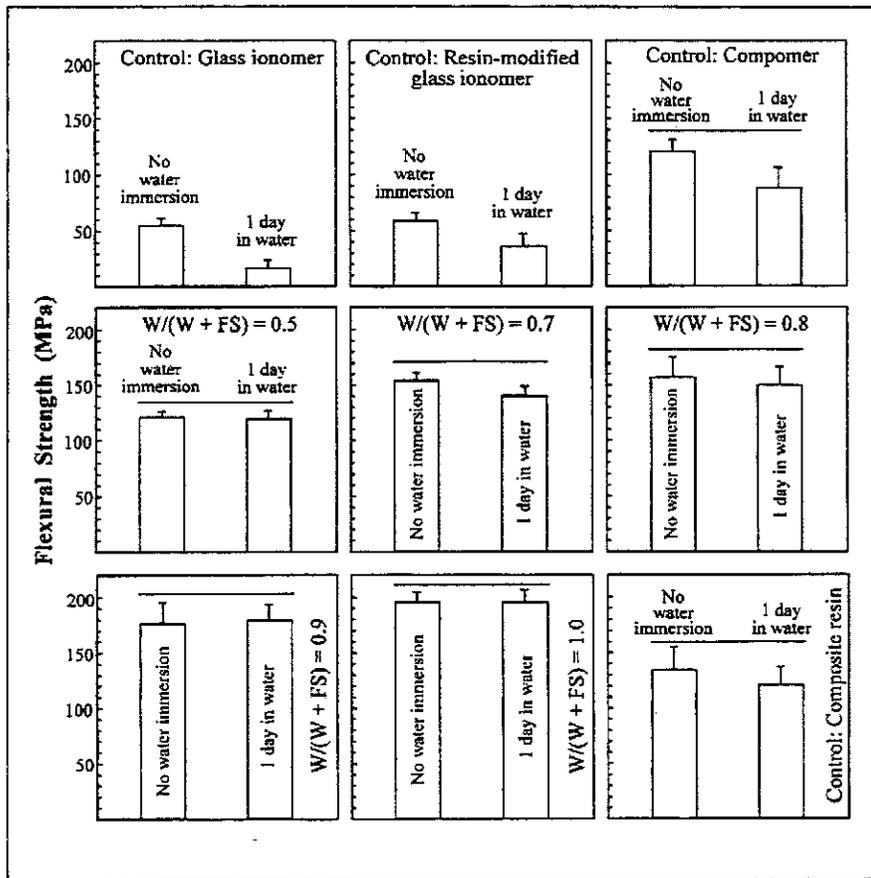


Figure 1. Flexural strength (mean ± sd; n = 6) of the four control materials and the whisker composites at whisker/(whisker = fluorosilicate glass) mass fractions of 0.5, 0.7, 0.8, 0.9, and 1.0. "W/(W + FS)" designates whisker/(whisker + fluorosilicate glass) mass fraction. In each plot, the first bar is strength of specimens without water immersion, and the second bar is strength of specimens after a one-day immersion in water. Horizontal lines indicate strength values that are statistically similar (p > 0.1; Student t). Only the glass ionomer and the resin-modified glass ionomer had a significant strength loss after a one-day water immersion.

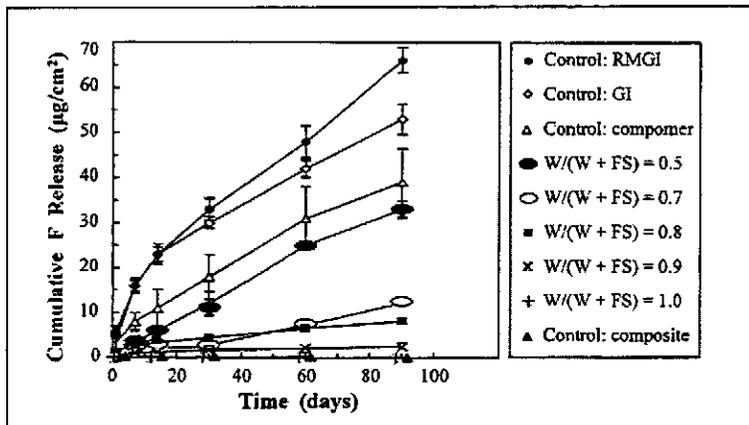


Figure 2. Fluoride release (mean ± sd; n = 4) versus storage time in distilled water of the four control materials and the whisker composites at whisker/(whisker = fluorosilicate glass) mass fractions of 0.5, 0.7, 0.8, 0.9, and 1.0. "RMGI" designates resin-modified glass ionomer, "GI" designates glass ionomer, and "W/(W + FS)" designates whisker/(whisker + fluorosilicate glass) mass fraction.

similar materials (Prosser & others, 1986; Mathis & Ferracane, 1989; Mitra & Kedrowski, 1994; Ferracane & Mitchem, 1994). The flexural strength values of the whisker composites were a few times higher, and the work-of-fracture values were orders of magnitude greater than those of the traditional glass ionomer and the resin-modified glass ionomer. The amount of fluoride release by the whisker-fluorosilicate composites was less than that of the traditional glass ionomer and the resin-modified glass ionomer. The minimum amount of fluoride release required to effectively inhibit secondary caries is yet to be determined clinically. A previous study (Swift, 1989b) showed that the fluoride concentration of a fluoride-releasing composite (Heliomolar) was only about 4% of that of a traditional glass ionomer (Ketac-Fil). However, significantly less demineralization was observed in teeth restored with Heliomolar (Arends, Ruben & Dijkman, 1990). The whisker composites of the present study had a cumulative fluoride release after 90 days of storage as high as 62% of that of a traditional glass ionomer, depending on the whisker/(whisker + fluorosilicate glass) mass fraction. Further studies should investigate the fusion of fluorosilicate glass particles, instead of silica, onto the whiskers, thereby possibly increasing the amount of fluoride release of the whisker composites while maintaining the superior mechanical properties.

The present study investigated the mechanical properties of composite specimens without water immersion and with one day of immersion in water at 37°C. Further studies should evaluate the long-term water-aging behavior of these composites, including water absorption, solubility, and durability of the mechanical properties. Ongoing studies on selected whisker composites indicate that the composite strength decreased after prolonged water aging, similar to that of current composite resins. Additional research is required to systematically understand the reinforcement mechanisms and to improve the water-aging resistance of the whisker-reinforced resin-carboxylic composites. Further studies should also aim at approximating the refractive index values of the phases to improve the translucency and esthetics of the composites. In addition, the wear behavior of the composites against enamel has yet to be investigated.

CONCLUSIONS

Ceramic whiskers can significantly reinforce composites containing fluorosilicate glass in a matrix formed from a resin that was modified with a carboxylic acid monomer. The composite mechanical properties and the amount of fluoride release can be adjusted for specific applications by tailoring the whisker:fluorosilicate glass ratio and the resin:carboxylic acid monomer ratio. The sizes of the whiskers are orders of magni-

tude smaller than available glass fibers, allowing for a relatively uniform distribution in the matrix. Depending on the ratio of whisker:fluorosilicate glass and resin:carboxylic acid monomer, the whisker composite releases fluoride up to 60% of that of a traditional glass ionomer. The flexural strength and work-of-fracture (or toughness) values of the whisker-fluorosilicate composites are significantly higher than those of a traditional glass ionomer, a resin-modified glass ionomer, and a compomer.

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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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