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Hydrothermal and Mechanical Stresses Degrade Fiber–Matrix Interfacial Bond Strength in Dental Fiber-Reinforced Composites

Serge Bouillaguet,[1] Andrea Schütt,[2] Pasi Alander,[3] Patrick Schwaller,[4] Gerhard Buerki,[4] Johann Michler,[4] Maria Cattani-Lorente,[2] Pekka K. Vallittu,[3] Ivo Krejci[1]

[1] Department of Cariology and Endodontology, School of Dental Medicine, University of Geneva, Geneva, Switzerland

[2] Department of Prosthodontics, School of Dental Medicine, University of Geneva, Geneva, Switzerland

[3] Department of Prosthetic Dentistry and Biomaterials Research, Institute of Dentistry, University of Turku, Turku, Finland

[4] EMPA, Materials Science and Technology, Thun, Switzerland

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Abstract: Fiber-reinforced composites (FRCs) show great promise as long-term restorative materials in dentistry and medicine. Recent evidence indicates that these materials degrade *in vivo*, but the mechanisms are unclear. The objective of this study was to investigate mechanisms of deterioration of glass fiber–polymer matrix bond strengths in dental fiber-reinforced composites during hydrothermal and mechanical aging. Conventional three-point bending tests on dental FRCs were used to assess flexural strengths and moduli. Micro push-out tests were used to measure glass fiber–polymer matrix bond strengths, and nanoindentation tests were used to determine the modulus of elasticity of fiber and polymer matrix phases separately. Bar-shaped specimens of FRCs (EverStick, StickTech, and Vectris Pontic, Ivoclar-Vivadent) were either stored at room temperature, in water (37 and 100°C) or subjected to ageing (10^6 cycles, load: 49 N), then tested by three-point bending. Thin slices were prepared for micro push-out and nanoindentation tests. The ultimate flexural strengths of both FRCs were significantly reduced after aging ($p < 0.05$). Both water storage and mechanical loading reduced the interfacial bond strengths of glass fibers to polymer matrices. Nanoindentation tests revealed a slight reduction in the elastic modulus of the EverStick and Vectris Pontic polymer matrix after water storage. Mechanical properties of FRC materials degrade primarily by a loss of interfacial bond strength between the glass and resin phases. This degradation is detectable by micro push-out and nanoindentation methods. © 2005 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 76B: 98–105, 2006

Keywords: adhesion; dental/craniofacial material; *in vitro*; mechanical properties; fiber-reinforced polymers

INTRODUCTION

Fiber-reinforced composites (FRCs) are used in dentistry to fabricate the frameworks of fixed partial dentures.[1–3] FRCs consist of reinforcing fibers embedded in a resin polymerized matrix. Monomers used to form the resin matrix are typically bifunctional methacrylates, like *bis*-phenyl-A-glycidyl-methacrylate (BisGMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA). Semiinterpenetrating polymer networks (semi-IPN) in polymer matrixes of dental FRCs have been used to diminish the brittle nature of highly crosslinked dimethacrylate polymers and to increase toughness.[4,5] Although different types of reinforcing fibers have been used, silanated glasses are preferred for their favorable mechanical properties, aesthetic qualities, and their ability to chemically bond to the polymer matrix.[6–9]

The mechanical behavior of FRCs is complex compared to monophasic materials or particulate-filled composite materials. These complexities result from the issue of fiber orientation, which can change an FRC′s properties from isotropic to orthotropic and anisotropic.[10] For dental applications, continuous longitudinal fiber orientation is used because longitudinal fibers exhibit superior mechanical properties along their long axes and can be specifically oriented to resist predominant oral stresses.[11] Increasing the percentage volume of fibers or adding bidirectionally oriented woven glass fibers increases the mechanical properties of fiber-reinforced

Correspondence to: S. Bouillaguet (e-mail: serge.bouillaguet@medecine.unige.ch)
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polymers.[12,13] However, a higher fiber content does not always result in higher mechanical properties, suggesting that parameters like resin-fiber impregnation and adhesion also are important factors.[14] Preimpregnation of fibers with resin allows the matrix to maximally wet the surface of the fibers and reduces the presence of voids that concentrate stress under load. Impregnation of fibers by the resin also decreases water sorption, which has been reported to reduce the elastic modulus of FRC materials.[15,16] Another factor that may contribute to the degradation of FRC materials under clinical conditions is mechanical loading. Drummond and Bapna reported significantly lower (30–38%) flexural strength of S2-glass reinforced FRC specimens after mechanical fatigue.[17] Although a durable adhesion between fibers and the polymer matrix is mandatory to ensure an efficient stress transfer between phases of the material, little attention has been paid to the effect of hydrothermal and mechanical stress on the fiber–polymer matrix interfacial bond strength.

A number of techniques have been developed to measure the micromechanical properties of fiber–polymer matrix interfaces. These methods include the push-out test, the pull-out test, the microbond test, and the single-fiber fragmentation test.[18–22] As each of these tests require specific specimen configurations and loading geometries, they are not all easily relevant to dental FRCs. Among these, the fiber push-out test is one of the most convenient techniques for describing interfacial properties. In dental FRCs, application of this test would make it possible to probe individual fibers within a bulk of a composite, immediately after fabrication and after mechanical or chemical aging. Micro push-out tests have not been applied to dental FRC materials previously.

Nanoindentation is used to measure mechanical properties of a material or a tissue on the submicron scale. Applications have included measurements of elastic modulus of metals, glasses, ultrahigh-molecular-weight polyethylene and modulus across the dentin–enamel junction in teeth.[23–26] It is therefore suggested that nanoindentation would be a useful technique to measure local mechanical properties of fiber and matrix phases within FRC materials.

The objective of this study was to use micro push-out tests to assess glass fiber–polymer matrix bond strengths of dental FRCs subjected to hydrothermal and mechanical aging. Specifically, the ability of aqueous media, with or without cyclic loading, to compromise fiber-matrix bonds was assessed. In addition nanoindentation was used to assess modulus of elasticity of fiber and polymer matrix phases. The utility of these newer tests was verified by comparing the results to conventional three-point flexural strengths and bulk moduli.

MATERIALS AND METHODS

Specimen Preparation

Two types of preimpregnated silanated glass fibers used clinically were evaluated: *EverStick* (ES, StickTech, Turku, Finland), consisting of continuous longitudinal silanated E-glass fibers preimpregnated in a Bis-GMA monomer-polymethylmethacrylate resin; and *Vectris Pontic* (VP, Ivoclar-Vivadent, Schaan, Liechtenstein), containing continuous longitudinal silanated R-glass fibers pre-impregnated with UDMA monomer resin. A total of 52 rectangular-bar specimens were prepared with the use of a stainless-steel mold ($2 \times 2 \times 25$ mm^3). The unpolymerized fiber prepregs were cut to a length of 25 mm, placed into the mold, covered by clear polyethylene sheets, and condensed between two glass plates located on both sides. To fill the excess space of the mold after placing the ES prepreg, a photopolymerizable resin of bis-GMA-TEGDMA (Stick Resin, Stick Tech Ltd, Turku, Finland) was added. For the VP specimens, a 25-mm-long prepreg was placed into the mold without additional resin.

ES specimens were photopolymerized for 20 s on both sides (Optilux Demetron 501, KerrHawe SA, Biaggio, Switzerland) and then postpolymerized at 80°C for 15 min (Liculite, DeTrey-Dentsply, Konstanz, Germany). According to the manufacturer, VP specimens were photopolymerized under vacuum in the VS1 framework former for 10 min and then postpolymerized for 20 min at 95°C in the Targis Power device (all from Ivoclar-Vivadent, Schaan, Liechtenstein). After polymerization, all specimens were dry polished with SiC paper (FEPA grit 800, 1200). After inspection for gross flaws, the specimens were randomly divided into four groups ($n = 6$). The first group was stored 1 week at room temperature in a dry environment *(dry)*. The second group was immersed for 1 month in distilled water at 37°C (*water*). This period of time was adequate to allow water sorption and hydrolytic degradation to occur.[15] The third group combined aqueous aging and cyclic loading (*cycled*). Cycled specimens were submitted to 1,000,000 cyclic stress at 1 Hz with a maximum loading force of 49 N. During mechanical loading, the specimens were simultaneously thermocycled between 5 and 55°C. This test was performed over 2 weeks, which simulated 5 years of clinical service.[27] The fourth group of specimens was immersed for 16 h in boiling water (100°C) (*boiled*) to test hydrolytic degradation.[28]

Three-Point Bending Test

Specimens ($n = 4$) were loaded to failure with the use of a conventional three-point bending test.[29] All samples were tested in a universal testing machine (Instron 1114, Instron Corp., High Wycomb, England). The span length was 20 mm and the crosshead speed was set at 0.5 mm/min; fracture load of the specimens was measured. Flexural strength (σ) and flexural modulus (E) were calculated from the formulas:

$$\sigma = 3Fl/2bh^2, \qquad E = Sl^3/(4bh^3)$$

where l is the span length, b the width, and h the height of the specimen. F is the registered force. S is the stiffness, $S = F/d$ (N/m), and d is the deflection corresponding to a load F at a point in the straight-line portion of the stress–strain curve.

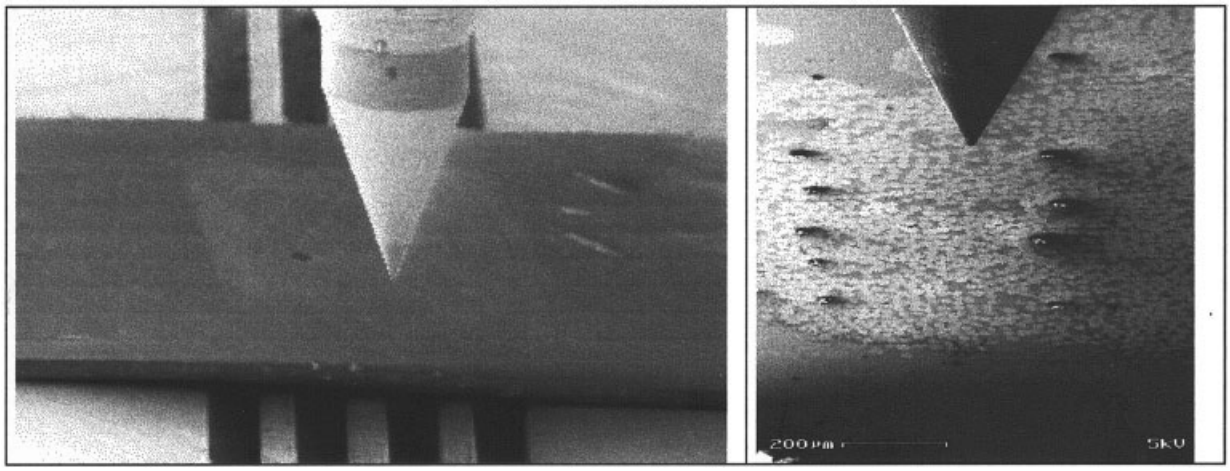

Figure 1. SEM images of the micro push-out test setup. The FRC material is embedded in PMMA resin and placed over the aluminum holder inside the SEM (left). The aluminum holder contains four grooves (width: 250 μm) to allow the fibers to be extruded during testing. The picture on the right shows the different locations randomly selected within the specimen where the different tests have been performed.

Determination of Fiber Content

The quantity of fibers in the FRCs was determined by combustion of the resin matrix ($n = 2$) for 45 min at 700° and measuring the weight of the specimens before and after combustion. The fiber content in vol % was calculated with the following formula:

$$V_f = (W_f/p_f)/(W_f/p_f + W_r/p_r),$$

where W_f is the weight proportion of glass fibers, p_f the density of the fibers (E glass = 2.54 g/cm^3, R glass = 2.53 g/cm^3), p_r the density of the resins (EverStick resin: 1.22 g/cm^3, Vectris resin: 1.26 g/cm^3) and W_r the weight proportion of the resin.

Micro Push-Out Test

Micro push-out tests were used to measure the interfacial bond strength between the reinforcing fibers and cured resins. Specimens ($n = 2$) were prepared for the micro push-out test, and 10 measurements were made on each specimen. The sites tested were nonadjacent and the fibers selected at random. For testing, specimens were embedded in PMMA resin (Technovit 4071, Hereaus Kulzer, Germany) and sliced perpendicularly to the long axis of the fibers (0.5 mm thick, Isomet, Buehler LTD, Lake Bluff, IL). The slices were fixed with sticky wax onto a polishing holder (Fischione Instruments Inc., Model 160, Evry, France) and wet ground (SiC papers 500–4000 grit) to a thickness of 100 μm using a Struers LaboPol-2 polishing machine (Struers, Birmensdorf, Switzerland). Each slice was then mounted on a grooved aluminum stub and placed on the SEM stage (DSM 962, Carl Zeiss AG, Feldbach, Switzerland) to perform fiber push-out tests. The fiber diameter-to-specimen thickness ratio and the width of the grooves were carefully chosen to prevent excessive specimen bending during loading (Figure 1).

The SEM instrument was equipped with a screw-driven microindenter with a displacement rate of 0.31 μm/s and a maximum load of 150 g (Touchstone Research Laboratory Ltd.). A conical diamond probe with a flattened end of 7 μm was used to apply the load to the fiber (Gyger AG, Thun, CH). The interfacial bond strength between the fibers and the matrix was determined by loading a single fiber until it protruded out of the matrix. The average debonding strength was calculated from the load data and measurements of the specimen geometry. The following equation was used to analyze the data:

$$\vartheta = L/(\pi\, Dt)$$

(ϑ is the debonding strength, L is the debonding load, D is the fiber diameter, and t the thickness of the specimen)

Nanoindentation Test

As a pilot method, the nanoindentation was used to support the hypothesis that aging did not simply plasticize the resin phase. Nanoindentation was used to measure the moduli of both the fibers and the resin matrices from FRCs with an MTS nanoindenter XP (MTS Systems corporation, Oak Ridge, TN) equipped with a three-sided pyramidal Berkovich indentation tip. During testing, the indenter was pressed onto the specimen while the applied load and the penetration into the surface were continuously measured during the loading and unloading cycle. Ten measurements were made on each specimen. For all nanoindentation experiments, the maximal load applied was set to 4 mN, which resulted in maximal penetration depths of about 800 nm. The unloading part of the loading curve was considered to be a purely elastic process,

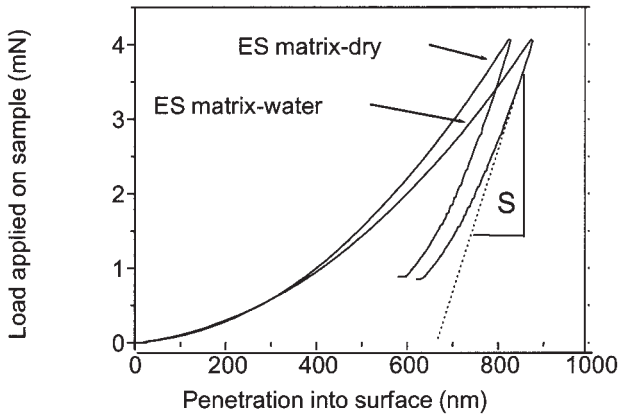

Figure 2. Nanoindentation load-penetration curves for ES matrix-dry and EverStick matrix stored in water for 1 month. The curve shows a slight plasticization of the EverStick matrix after water storage.

and used models based on the elastic contact theory to calculate the so-called unloading stiffness, S (Figure 2). From S, the Young's modulus $E_{(\text{indent})}$ was calculated with the use of the methods of Oliver and Pharr.[30]

Statistical Analysis

Ultimate flexural strength measurements and flexural moduli were compared with the use of one-way ANOVA. Micro push-out data were first compared with the use of a one-way ANOVA. Because each specimen yielded multiple bond strength measurements (ca. 10 measures per specimen), the average matrix–fiber bond strength was calculated for each sample, and the means among samples were compared with the use of ANOVA. Because this ANOVA showed no statistically significant differences among the means ($p > 0.05$), the individual measurements within each sample were treated as independent measurements. The Fisher's least-significant-difference procedure was used to determine statistical differences between the means ($p < 0.05$). Nanoindentation data were not subjected to statistical analysis because only one specimen per group was used for the measurements. However, the precision of the test was calculated from the 10 measurements made on each specimen.

RESULTS

Three-Point Bending Test

Hydrothermal and mechanical aging decreased the flexural strength of the specimens (Figure 3). The mean flexural strength of ES specimens stored in air was 1150 MPa. Flexural strengths significantly decreased to 850 MPa after mechanical loading and immersion in boiling water for 24 h (669 MPa). Water storage also reduced flexural strength (to 759 MPa), although this reduction was not significantly different. The mean flexural moduli of ES specimens ranged from 26.2 (dry) to 23.8 GPa (boiled) (Table I). All other aging treatments decreased the stiffness of the ES material, but were not statistically from unaged controls.

For the VP material, both mechanical loading and water storage significantly reduced the flexural strength of the specimens, which dropped from 1005 MPa (dry) to 746 and 756 MPa, respectively. The mean flexural strength of the boiled specimens was also significantly reduced (722 MPa). The mean flexural moduli of VP specimens ranged from 38.6 (boiled) to 28.7 GPa (cycled). Mechanical and hydrothermal aging significantly decreased the flexural modulus of VP, whereas the boiled specimens were significantly stiffer (Table I).

Fiber Content

The mean inorganic filler contents in the FRC specimens were 42.3% for the ES and 41.7% for the VP materials.

Micro Push-Out Test

Hydrothermal and mechanical aging decreased interfacial bond strength for both materials (Figure 4). For ES (dry), the mean interfacial bond strength was 100 (± 9) MPa. Boiling as well as water storage significantly reduced fiber-matrix bond strengths to 78 ± 10.5 MPa and 78.8 ± 6.8 MPa, respectively. The same effect was observed for the specimens subjected to mechanical and hydrothermal aging (85.5 ± 8.5 MPa). A representative load-displacement curve for a dry ES specimen is shown in Figure 5. The SEM images illustrate the different phenomena observed during testing. The curve shows progressive bending of the specimen under initial load. The load increased continuously (from A to B) until the first cracks appeared at the fiber–matrix interface. The corresponding SEM picture (B) shows a slight curling of the resin matrix around the loaded fiber. Then the load reached a maximum value (C) corresponding to the complete debonding of the fiber from the resin matrix.

For the VP specimens, there was a significant reduction in fiber–matrix bonds in specimens stored in water (65.5 ± 9.1 MPa) or aged (64.5 ± 4.3 MPa) compared to the dry speci-

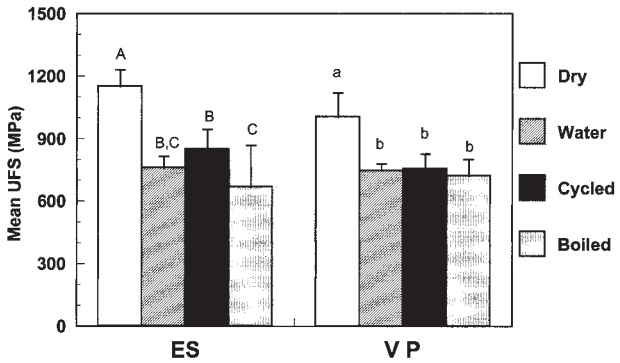

Figure 3. Ultimate flexural strengths of ES and VP specimens measured by three-point bending tests ($n = 4$). For each material and condition, means denoted by the same letter are not statistically different (Fisher's least-significant-difference procedure, $p < 0.05$).

TABLE I. Mean E Modulus for Each Material and Condition Calculated from the Results of the Three-Point Bending Test (mean/SD in GPa). Means Followed by the Same Letter are not Statistically Different ($p < 0.05$)

	Dry	Water	Cycled	Boiled
ES	26.2 ± 2 (A)	25.5 ± 2.5 (A)	25.8 ± 5.1 (A)	23.8 ± 3.1 (B)
VP	32.7 ± 2.4 (a)	30.9 ± 0.8 (b)	28.7 ± 1.7 (b)	38.6 ± 2 (c)

mens (74.1 ± 5.8 MPa). Because all fibers fractured prematurely during testing, no data were collected for the boiled VP specimens.

Nanoindentation Test

Pilot data suggested that the indentation modulus $E_{(indend)}$ of the ES polymer matrix was the same for the dry and cycled specimens (Table II). Water storage caused a slight reduction in the $E_{(indend)}$ of the polymer matrix, whereas the boiling increased $E_{(indend)}$. For example, Figure 2 shows load-penetration curves for the dry ES polymer matrix and water-immersed ES polymer matrix. A slightly deeper penetration was observed for the water-immersed polymer matrix compared to the dry polymer matrix. Except for the cycled specimens, the $E_{(indend)}$ modulus of the glass fibers of the ES did not change. For the VP specimens, water storage and cyclic loading reduced the $E_{(indend)}$ modulus of the resin matrix (Table II). Water storage also decreased the $E_{(indend)}$ modulus of the glass fibers of the VP material.

DISCUSSION

Although the three-point bending test is commonly used to estimate the mechanical properties of composite materials, it has several limitations with regard to FRC materials. Large (e.g., $25 \times 2 \times 2$ mm^3) beam specimens are more susceptible to flaws that can significantly influence the results of three-point bending tests.[31] Additionally, the calculation of the ultimate failure strength may be problematic because FRC beams do not fail abruptly under load.[14] Finally, the ratio between the span length and the height of the specimen influences the stiffness calculated with the standard flexure formula.[32] Thus, the three-point bending data need to be taken with these limitations in mind.

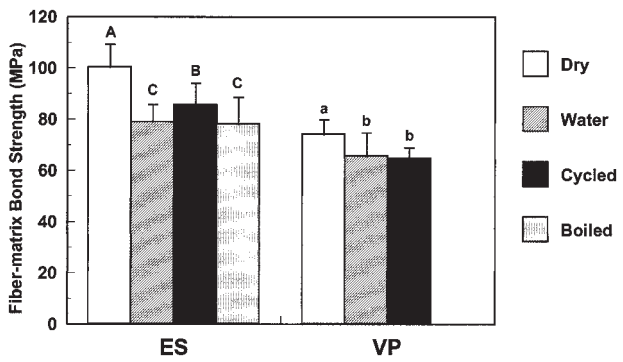

Figure 4. Mean interfacial bond strengths between the reinforcing fibers and the polymer matrix of ES and VP measured by micro push-out tests ($n = 20$). For each material and condition, means denoted by the same letter are not statistically different (Fisher's least-significant-difference procedure, $p < 0.05$).

Typical flexural strengths for FRCs range from 500 to 1000 MPa, depending on the sample geometry and fiber content.[33] In the current study, the three-point bending test gave comparable results for flexural strengths and bulk moduli before aging (Table I, Figure 3). The high fiber content and strategies to ensure maximal polymerization likely account for the high strength obtained for both materials in the current study. However, aging reduced the flexural strength of both FRC materials by almost 30%. The results of the current test agreed with those previously published on similar materials.[14]

The quality of the interface between the reinforcing fibers and the resin matrix affects the mechanical performance of FRC materials.[34] Without adequate adhesion between these phases, the fibers act as voids in the resin matrix, thereby weakening the FRC. The micro push-out tests showed a strong adhesion between the resin matrix and the glass fibers for dry specimens, which is in agreement with previously published data on E glass/epoxy interfaces.[35] For these materials, adhesion was promoted with the use of silane coupling agents, which are known to maximize chemical and physical bonding between the different components within composite materials.[36]

The current data show a definite drop in bonding performance after water storage, indicating that the interfacial bond strength between the reinforcing fibers and the resin matrix may be compromised during hydrothermal aging (Figure 4). The drop of 15–20% in aged interfacial bond strengths agrees to some degree with the reduction observed with the three-point bending test after aging (Figure 3). Although a plasticization of the resin matrix has frequently been proposed as an explanation for the reduction in mechanical properties of FRCs aged in water, the current observations indicate that a loss of interfacial bond strength is a primary cause of lowered mechanical properties. A partial hydrolysis of the silane bonds formed between the glass fibers and the matrix may explain this result.[37] Furthermore, the degradation of the glass fiber itself cannot be ruled out, because glasses also are susceptible to hydrolytic degradation.[37] Future studies will be necessary to dissect the contribution of these mechanisms to the loss of bulk strength.

Mechanical loading also decreased the interfacial bond strength to levels that were similar levels to those of specimens stored 1 month in water. Although both aging processes were quite different in terms of duration, mechanical aging

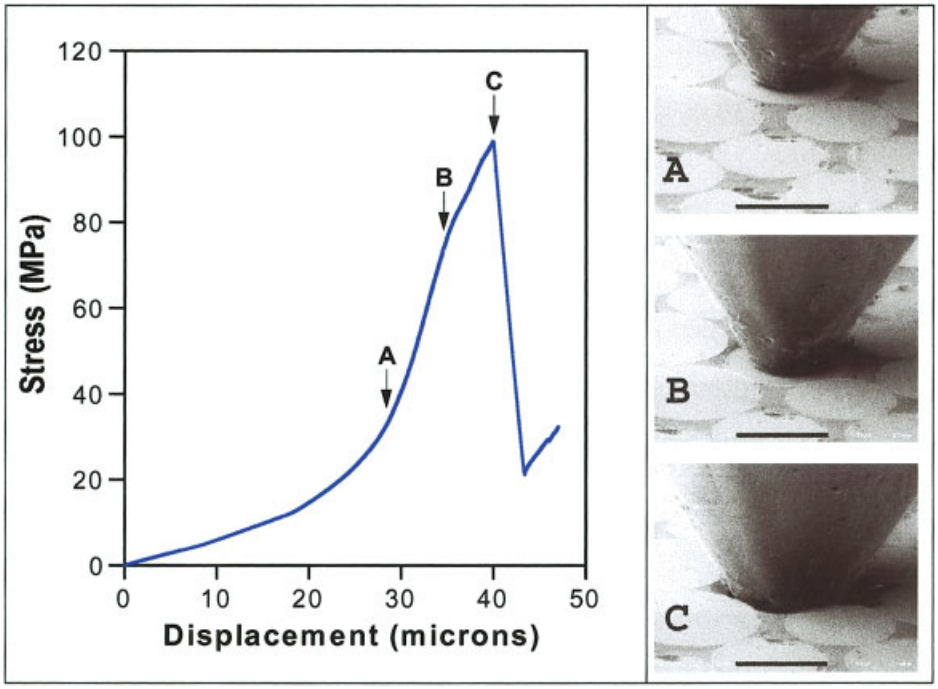

Figure 5. The figure shows a typical load-displacement curve of a micro push-out test (left) and corresponding SEM images (right) showing the diamond tip of the indenter pushing out a single fiber. The curve shows the bending of the specimen on the SEM holder under the pressure of the indenter (picture A, also indicated on curve). At point B (also picture B), the first cracks develop along the fiber–matrix interface until the complete failure occurs at C (picture C). Full debonding of the fiber was always characterized by a sudden drop in stress and always occurred before any contact between the tip of the indenter and the resin matrix. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

also was performed in a wet environment. Furthermore, the repeated loading of the specimens may have crushed or stretched the fibers, which in turn could have weakened the fiber–matrix interfaces. Immersion in boiling water also decreased interfacial bond strength for the ES specimens. This result is in agreement with a previous report suggesting that structural changes might occur at the polymer matrix–fiber interface because of different coefficients of thermal expansion of fiber and polymer matrix.[38] Surprisingly, the glass fibers of VP exhibited brittle fracture behavior during testing, which prevented producing micro push-out data. In this case, the compression strength of the glass fiber may have been altered by the boiling process. Although the micro push-out test was successful for characterizing fiber–matrix interfacial properties, the data presented in this study rely on simplified stress-based schemes that do not take into account the complicated stress states surrounding the fibers and the complex phenomena that occur during debonding of the fiber.[39]

The results of the nanoindentation tests further support interfacial degradation rather than plasticization of resin matrix as the principle mechanism in the aqueous degradation of FRCs. Even though no statistical evidence was available, the precision of the measurements was excellent (Table II). The nanoindentation test revealed marked differences in moduli between fibers and matrix. Whereas a moduli of 5–7 GPa was found for both resin matrices, the moduli of the glass fibers was 75 GPa. These results are in agreement with previously published data.[35] As expected, the semiinterpenetrating polymer network structure of ES had a lower E modulus than that of highly crosslinked polymer matrix of VP. The resin phase did not change after aging, but there was a trend toward a slight softening of the polymer matrix of VP after water

TABLE II. Elastic Moduli of Fibers and Matrix of EverStick (ES) and Vectris Pontic (VP) Calculated from the Nanoindentation Tests. Each Data Represents the Mean Value Calculated from 10 Measurements Made on the Same Sample

	ES		VP	
$E_{(\text{Indend})}$ Modulus	Matrix	Fibers	Matrix	Fibers
Dry	4.9 ± 0.2	76.8 ± 3.6	7.2 ± 0.9	76.9 ± 9.9
Water	4.3 ± 0.2	77.3 ± 2.6	5.2 ± 0.2	69.3 ± 5.9
Cycled	5.1 ± 0.2	68.5 ± 5.3	5.0 ± 0.3	75.6 ± 4.2
Boiled	6.0 ± 0.4	78.5 ± 3.9	7.1 ± 1.0	78.8 ± 4.5

immersion and cyclic mechanical loading. However, the specimens were partially dehydrated before nanoindentation, which would have masked the plasticizing effect of water on the matrix. A lack of plasticization may also be attributed to the preimpregnation of the reinforcing fibers with resins, which favored the production of void-free specimens. Previous reports have correlated the presence of voids inside FRC materials with water uptake.[16] The nanoindentation test also revealed that aging did not change the moduli of the glass fibers, although a slight deterioration was observed for the glass fibers in cycled ES and VP after water storage. This deterioration remains to be explained.

In summary, the current study demonstrated that mechanical properties of two commonly used FRC materials degrade after hydrothermal or mechanical aging. The micro push-out test successfully identified and characterized the changes occurring at the fiber–resin interface, whereas the nanoindentation test gave supporting information about the degradation of the resin matrices. These changes were consistent with changes in the bulk mechanical properties measured by three-point bending tests.

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REFERENCES

1. Freilich MA, Meiers JC. Fiber-reinforced composite prostheses. Dent Clin North Am 2004;48:545–562.
2. Freilich MA, Meiers JC, Duncan JP, Eckrote KA, Goldberg AJ. Clinical evaluation of fiber-reinforced fixed bridges. J Am Dent Assoc 2002;133:1524–1534.
3. Bouillaguet S, Schütt A, Marin I, Etechami L, Di Salvo G, Krejci. Replacement of missing teeth with fiber-reinforced composite FPDs: clinical protocol. Pract Proced Aesthet Dent 2003; 15:195–202.
4. Lastumäki T, Lassila LVJ, Vallittu PK. The semi-interpenetrating polymer network matrix of fiber-reinforced composite and its effect on the surface adhesive properties. J Mater Sci Mater Med 2003;14:803–809.
5. Kallio TT, Lastumäki TM, Vallittu PK. Effect of application time on bond strength of polymer substrate repaired with particulate filler composite. J Mater Sci Mater Med 2003;14:999–1004.
6. Ellakwa AE, Shortall AC, Marquis PM. Influence of fiber type and wetting agent on the flexural properties of an indirect fiber reinforced composite. J Prosthet Dent 2002;88:485–490.
7. McDonough WG, Antonucci JM, Dunkers JP. Interfacial shear strengths of dental resin-glass fibers by the microbond test. Dent Mater 2001;17:492–498.
8. Bae JM, Kim KN, Hattori M, Hasegawa K, Yoshinari M, Kawada E, Oda Y. The flexural properties of fiber-reinforced composite with light-polymerized polymer matrix. Int J Prosthodont 2001;14:33–39.
9. Kallio TT, Lastumaki TM, Vallittu PK. Bonding of restorative and veneering composite resin to some polymeric composites. Dent Mater 2001;17:80–86.
10. Dyer SR, Lassila LVP, Jokinen M, Vallittu PK. Effect of fiber position and orientation on fracture load of fiber-reinforced composite. Dent Mater 2004;20:947–955.
11. Vallittu PK. Flexural properties of acrylic resin polymers reinforced with unidirectional and woven fibers. J Prosthet Dent 1999;81:318–326.
12. Kennedy KC, Chen T, Kusy RP. Behaviour of photopolymerized silicate glass fibre-reinforced dimethacrylate composites subjected to hydrothermal ageing. Part II. Hydrolytic stability of mechanical properties. J Mater Sci Mater Med 1998;9:651–660.
13. Kim SH, Watts DC. Effect of glass-fiber reinforcement and water storage on fracture toughness (KIC) of polymer-based provisional crown and FPD materials. Int J Prosthodont 2004; 17:318–322.
14. Behr M, Rosentritt M, Lang R, Handel G. Flexural properties of fiber reinforced composite using a vacuum/pressure or a manual adaptation manufacturing process. J Dent 2000;28:509–514.
15. Vallittu PK. Effect of 180-week water storage on the flexural properties of E-glass and silica fiber acrylic resin composite. Int J Prosthodont 2000;13:334–339.
16. Chai J, Takahashi Y, Hisama K, Shimizu H. Water sorption and dimensional stability of three glass fiber-reinforced composites. Int J Prosthodont 2004;17:195–199.
17. Drummond JL, Bapna MS. Static and cyclic loading of fiber-reinforced dental resin. Dent Mater 2003;19:226–231.
18. Chandra N, Ghonem H. Interfacial mechanics of push-out tests: Theory and experiments. Composites 2001;32A:575–584.
19. Janczak J, Bürki G, Rohr L. Interfacial characterization of MMCs and CMCs using a SEM-pushout technique. Key Eng Mater 1997;127–131;623–630.
20. Butler EP, Fuler ER, Chan HM. Interfacial properties for ceramic composites from single-fiber pull-out test. Mater Res Soc Symp Proc 1990;170:17–24.
21. Miller B, MuriI P, Rebenfeld L. Microbond A. Method for determination of the shear strength of a fiber–resin interface. Compos Sci Technol 1987;28:17–32.
22. Zhou XF, Wagner HD, Nairn JA. Fiber-matrix adhesion from the single-fiber composite test: nucleation of interfacial debonding. Composites 1999;30A:1387–1400.
23. Bei H, Lu ZP, George EP. Theoretical strength and the onset of plasticity in bulk metallic glasses investigated by nanoindentation with a spherical indenter. Phys Rev Lett 2004;93:125504.
24. Gilbert JL, Merkhan I. Rate effects on the microindentation-based mechanical properties of oxidized, crosslinked, and highly crystalline ultrahigh-molecular-weight polyethylene. J Biomed Mater Res 2004. Forthcoming.
25. Yu N, Polycarpou AA, Wagoner Johnson AJ. Measuring mechanical properties of fine-wire cross-sections used in medical devices. J Biomed Mater Res 2004;70B:106–113.
26. Marshall GW Jr, Balooch M, Gallagher RR, Gansky SA, Marshall SJ. Mechanical properties of the dentinoenamel junction: AFM studies of nanohardness, elastic modulus, and fracture. J Biomed Mater Res 2001;54:87–95.
27. Krejci I, Lutz F. *In-vitro* test results of the evaluation of dental restoration systems. Correlation with *in-vivo* results. Schweiz Monatsschr Zahnmed 1990;100:1445–1449.
28. Ehrenstein GW, Schiemann A, Bledzki A, Spaude R. Corrosion phenomena in glass-fiber-reinforced thermosetting resins. In: Cheremisinoff NP, editor. Handbook of ceramics and composites. New York: Marcel Dekker; 1990. p 244.
29. Craig RG, Powers JM. Restorative dental materials (11th ed.). Mechanical properties. St. Louis: Mosby; 2002. Chap. 4, p 77–78.
30. Oliver WC, Pharr GM. Measurement of hardness and elastic modulus by instrumented indentation: advantages in understanding and refinements in methodology. J Mater Res 2004; 19:3–20.
31. Chung SM, Yap AUJ, Tsai KT, Yap FL. Elastic modulus of resin-based dental restorative materials: A microindentation approach. J Biomed Mater Res. Forthcoming.

32. Eckrote KA, Burstone CJ, Freilich MA, Messer GE, Goldberg AJ. Shear in flexure of fiber composites with different end supports. J Dent Res 2003;82:262–266.
33. Freilich MA, Meiers JC, Duncan JP, Goldberg AJ. Fiber-reinforced composites in clinical dentistry. Chapter 2: Composition, architecture and mechanical properties of fiber-reinforced composites. Chicago: Quintessence Publishing; 1999. p 18–46.
34. Vallittu PK. The effect of void space and polymerization time on transverse strength of acrylic-glass fibre composite. J Oral Rehabil 1995;22:257–261.
35. Zhou XF, Wagner HD, Nutt SR. Interfacial properties of polymer composites measured by push-out and fragmentation tests. Composites 2001;32A:1543–1551.
36. Matinlinna JP, Lassila LV, Ozcan M, Yli-Urpo A, Vallittu PK. An introduction to silanes and their clinical applications in dentistry Int J Prosthodont 2004;17:155–164.
37. Lassila LV, Nohrstrom T, Vallittu PK. The influence of short-term water storage on the flexural properties of unidirectional glass fiber-reinforced composites. Biomaterials 2002;23:2221–2229.
38. Jancar J, Dibenedetto AT, Goldberg AJ. Thermoplastic fiber-reinforced composites for dentistry. Part II: Effect of moisture on flexural properties of unidirectional composites. J Mater Sci Mater Med 1993;4:562–568.
39. Pisanova E, Zhandarov S, Mäder E. How can adhesion be determined from micromechanical tests? Composites 2001; 32A:425–434.