Interfacial shear strengths of dental resin-glass fibers by the microbond test

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Abstract

Objective: The aim of this study was to investigate the feasibility of using the microbond test (MBT) to probe the durability of the bond between a polymerized dental resin with differently silanized E-glass fibers.

Methods: The E-glass fibers were silanized with equivalent amounts of two types of acrylic-silane coupling agents: 3-methacryloxypropyltrimethoxysilane (MPTMS) and 10-methacryloxydecyltrimethoxysilane (MDTMS), a more hydrophobic silane coupling agent than MPTMS. Unsilanized E-glass fibers were used as the control. Microdroplets of a photo-activated dental resin were applied on the fiber and photocured with visible light irradiation (470 nm). Subsequently, the specimens were tested in shear after 24 h storage in air at 23°C or water at 60°C.

Results: The mean interfacial shear strength (τ) and the standard deviation in MPa for the three systems in 23°C in air ($n > 7$) were: 33.8(10.1), 33.7(8.9) and 15.3(4.2) for the MPTMS silanized, MDTMS silanized, and unsilanized fibers, respectively. When the three types of fibers were first exposed to 60°C water for 24 h prior to having the microdroplets of the resin bonded to them, the strength values of the MDTMS silanized fibers and the control fibers remained essentially unchanged at ($n \geq 7$) 31.8(7.7) and 17.5(4.9) MPa respectively; the MPTMS specimens showed a significant decrease to 15.8(4.8) MPa. Similar trends were observed when the fibers had microdroplets of the resin bonded to them prior to aqueous exposure.

Significance: These results indicate that the microbond test has the sensitivity to measure changes at the interface between polymerized dental resins and variously silanized E-glass fibers. It appears that surface modification of the fibers with the more hydrophobic silane coupling agent MDTMS promotes enhanced resistance to degradation from exposure to water. The microbond test has the potential for studying dental adhesion involving small bonded areas under a variety of conditions with different adhesive systems and substrates. Published by Elsevier Science Ltd on behalf of Academy of Dental Materials.

Keywords: Adhesion; Microbond test; Interface strength; Dental resins

1. Introduction

The quest for durable, aesthetic and bondable materials that can restore both the function and appearance of lost tooth structure has been a major concern for dental materials researchers. A significant advance, which ushered in the modern era of restorative dentistry, was the development of ambient temperature thermosetting acrylics reinforced with silanized glass [1–6]. For silica-reinforced polymeric composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler exerts a profound effect on the properties and durability of dental composites. This critical influence is due to the extensive surface area that the interface occupies in the composite microstructure, which can be as high as 3000 cm^2/cm^3 [7]. There is a

need for appropriate methods to assess changes in the strength and stability of the interface, because of its important role in determining mechanical properties and long-term durability of composites. Durability issues become important because the dental restoratives are constantly exposed to aggressive, aqueous environments that can attack all phases of the composite, with the most serious threat being the hydrolytically vulnerable silane-glass bond. It is important to increase our understanding of this critical interfacial phase so that appropriate strategies can be developed to enhance composite performance and durability by providing a better quality interface. In this study, we propose the use of the microbond test (MBT) to assess the strength and durability of this important silane-glass bonded interface.

In this test, a microdroplet of resin is placed on a single glass filament, embedding a length of approximately 150–200 μm. After polymerization, the polymer droplet is mechanically sheared off the fiber, and the interfacial

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shear strength is then calculated by dividing the force to debond the droplet by the area of contact between the droplet and the fiber [8]. By means of the MBT, a wide spectrum of resin systems, coupling agents and fillers can be screened for use in dental composites as well as other applications. Properly used, the MBT has the potential to be a sensitive, versatile and facile method for probing interfacial events in acrylic, epoxy, and other polymeric composites. The new knowledge provided by this single fiber technique should aid in the development of improved dental composites.

A hypothesis to be tested in this study is whether the MBT can be used in durability studies. Past studies on glass fibers have shown that E-glass fibers will degrade upon exposure to moisture [9]. Thus, there is a concern that the fibers may degrade so much that the MBT could not be performed. In this study, the MBT was used to assess the efficacy of two silane coupling agents, 3-methacryloxypropyltrimethoxysilane (MPTMS) and 10-methacryloxydecyltrimethoxysilane (MDTMS), before and after aqueous challenge. A second hypothesis to be tested in this study is that the longer hydrocarbon chain $[-(CH_2)_{10}-]$ silane, MDTMS, with its greater hydrophobicity, offers enhanced protection of the interface to aqueous challenges compared to the shorter, less hydrophobic $[-(CH_2)_3-]$silane, MPTMS.

2. Materials and methods

2.1. Glass fibers

E-glass fibers from Owens Corning (Toledo, OH, USA) were supplied with a proprietary water-soluble sizing. For this study, the sizing was removed by washing in distilled water. The composition of this E-glass on a mass fraction basis was (52.0–56.0)% SiO_2, (12.0–16.0)% Al_2O_3, (5.0–10.0)% B_2O_3, (16.0–25.0)% CaO, (0.0–5.0) %MgO, (0.0–2.0)% Na_2O-K_2O, (0.0–1.5)% TiO_2, (0.0–0.8)% Fe_2O_3, and (0.0–1.0)% F [10].

2.2. Resin systems

Commercially available materials were used to formulate the visible light activated resin system and to silanize the E-glass fibers. The monomers 2,2-bis [p-(2′-hydroxy-3′-methacryloxypropoxyphenyl)]propane, Bis-GMA (Freeman Chemical Corp., Port Washington, WI, USA), and triethylene glycol dimethacrylate, TEGDMA (Esstech, Essington, PA, USA) were used to prepare the resin. The resin was photo-activated by the addition of the photo-oxidant, camphorquinone (Aldrich Chemical Company, Inc., Milwaukee, WI, USA) and the photo-reductant, ethyl-4-N,N-dimethylaminobenzoate (4EDMAB) (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). The composition in mass fraction of the photo-active resin was: Bis-GMA:0.695, TEGDMA:0.295, CQ:0.02, and

4EDMAB:0.08. The silane coupling agents were 3-methacryloxypropyltrimethoxysilane (MPTMS; Aldrich Chemical Company, Inc., Milwaukee, WI, USA) and 10-methacryloxydecyltrimethoxysilane (MDTMS; Tokayama Corp., Tokyo, Japan).

2.3. Silanization of E-glass fibers

Three separate bundles of water-soluble sized E-glass fibers were first washed for 1 min in a stream of distilled water. A solution was prepared consisting of 285 mL methanol, 15 mL distilled water, and 1.5 g acetic anhydride as the silanization catalyst. The solution was divided into three equal parts in three 250 mL beakers. To two of these solutions was added, with magnetic stirring at 23°C, 1.03 g of MPTMS or 1.44 g of MDTMS. The masses chosen represent mole equivalents of silane. The third solution without the silane agent was used for the unsilanized E-glass fibers. The solutions were stirred for 3 h at 23°C. The MDTMS solution exhibited slight turbidity in contrast to the clear MPTMS solution. A bundle of E-glass fibers (Owens Corning, Granville, OH, USA) was then immersed in each of the three solutions (the solution that did not contain any silane agent serving as a control). After the fibers were allowed to soak for 24 h at 23°C, the solutions were heated on a hot plate in a hood (60–70°C) for 3 h until more than half the solvent had been evaporated. At this point, the fiber bundles were removed from solution, allowed to drain, inserted (using tweezers) into three separate graduate cylinders (100 mL), and then heated at 110°C under vacuum (2.7 KPa) for 1 h in a vacuum oven (Lab-Line Instruments, Inc., Model 3608, Melrose Park, IL, USA). The cylinders containing the dry fibers were removed and cooled to 23°C. Each cylinder was covered with tissue paper to minimize contamination of the fibers.

2.4. Preparation of microdrop specimens

In preparing the microdrop specimens, five fibers of MPTMS silanized E-glass (16 μm diameter fibers) were separated individually from a tow of fibers. These individual fibers were then attached to a specially built aluminum frame via double-sided tape. Subsequently, microdroplets of the previously photoactivated Bis-GMA/TEGDMA resin were put on the fibers using a thin glass rod. Three droplets were placed on each fiber, each separated by approximately 2.5 cm. Following this step, the microdroplets were photopolymerized in air by a 3 min exposure to blue light irradiation having a maximum emission at 470 nm (Triad 2000, Dentsply International Inc., York, PA, USA). After curing, the polymerized micro-droplets were stored at 23°C for 24 h in air. Then, sections approximately 2.5 cm long were cut from the fibers and attached individually to small aluminum tabs using double-sided tape (Fig. 1). Thus, for each tabbed sample, there was one droplet per fiber. Finally, the ends of the fibers were securely bonded to the tabs by application of a fast-setting epoxy (Hardman,
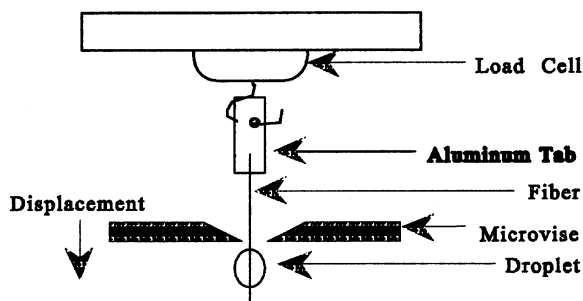
Fig. 1. Schematic of microbond test apparatus.

Division of Harcros Chemicals, Inc., Belleville, NJ, USA). This procedure was then repeated for the E-glass with the MDTMS silane and for the E-glass without silane. The reader should note that only droplets that had an embedded length ranging from 150 to 200 μm in order to reduce the potential effects of droplet size. Thus, not all of the specimens made were used.

Preliminary durability exposures were performed through two different routes. The first route was to expose the different fiber surfaces to immersion in 60°C distilled water for 24 h followed by drying the fibers for 24 h at 60°C in the vacuum oven (2.7 kPa). After the fibers had cooled to 23°C, resin droplets were applied and photo-bonded to the fibers following the procedure described above. This protocol should give an indication of the ability of the silane sizing itself to resist water. The second protocol involved making polymerized microdroplet specimens on the three groups of fibers. The resin bonded assemblies were then exposed to 60°C distilled water for 24 h, oven-dried for 24 h at 60°C and finally cooled to 23°C. This last protocol should give an indication of the ability of the interfacial region formed by polymerization of the resin-silane bonded fiber to resist moisture.

2.5. Interfacial shear testing of the microdroplets

The apparatus for testing the polymerized microdroplets is shown in Fig. 1. The tab is attached to a rod that is connected to a load cell (Mettler BB240, Mettler-Toledo, Inc., Columbus, OH, USA). The microvise (Mitutoyo, Tokyo, Japan) is then positioned just above the droplet to be tested and then closed to where the vise is almost touching the fiber. This step is important because there is concern that if the droplet is loaded at different points along its length, the stress pattern changes, thus introducing additional variability in the results [11]. During the test, the microvise applies a shear force to the droplet attached to the fiber through an actuator (Newport 850A, Newport Corporation, Irvine, CA, USA) at a rate of 16 μm/min. The change in load as a function of time is recorded on a computer and the shear strength to debond the polymerized microdroplet is calculated from the equation $\tau = F/(\pi D L)$ where τ is the interfacial shear strength, F is the applied load, D is the fiber diameter, and L is the length of the droplet along the fiber axis. If the fiber broke during the test, that test value was discarded from the calculation. The standard uncertainty in the load cell measurement is 0.01 g. The standard uncertainty in the measurement of bonded area dimensions is 1.9 μm for the droplet embedded length and 1.1 μm for the fiber diameter. The standard uncertainty in the speed of the actuator was 1.4 μm/min. The expanded uncertainty in the calculation of τ is therefore 1.74 MPa. When calculating this last uncertainty, it became clear that the uncertainty in measuring the fiber diameter was the largest source of uncertainty. Data were analyzed by analysis of variance (ANOVA) at a significance level of 0.05.

2.6. Infrared microspectroscopy

FT–IR microscopy was used to analyze the surfaces of the debonded areas after the polymerized microdroplets were sheared from the fibers and also to analyze the fibers with only silane. A Nicolet® Nic-Plan® (Madison, WI, USA) microscope attached to a Nicolet Magna 550® bench was used to analyze the E-glass fiber. The microscope was equipped with a liquid nitrogen cooled MCT-A detector and adjustable slit apertures above and below the focal plane. The apertures were closed to the fiber width and the desired length. Spectra were collected using the 32X objective (N.A. = 0.65) in transmission mode, with a resolution of 8 cm^{-1} and 256 co-added scans.

3. Results

When tested at 23°C without aqueous conditioning, both the MPTMS and MDTMS silanized fibers coupled well to polymerized microdroplets and gave similar mean τ values, 33.8 and 33.7 MPa, respectively (Table 1(a)). The mean τ values of these systems were significantly higher than the mean τ values obtained from bonding microdroplets to the unsilanized glass surfaces (15.3 MPa). However, when the three sets of fibers were first exposed to 60°C water and then (after drying and cooling to 23°C) had the resin microdroplets cured on the exposed fibers, the MDTMS system retained its interfacial shear properties as measured by its mean τ value of 31.8 MPa (Table 1(b)). The MPTMS system degraded to the point where its mean τ value (15.8 MPa) was similar to that for specimens prepared with the unsilanized fibers (17.5 MPa). As shown in Table 1(c), significant loss of τ even occurred when the polymerized microdroplet-fiber MPTMS specimens were fabricated from fibers not given prior conditioning in 60°C water, but then exposed to aqueous conditioning. The mean τ value for the MDTMS specimens was 30.5 MPa, compared to the mean τ values of 17.6 MPa for the MPTMS group, and 19.0 MPa for the unsilanized specimens. Two way ANOVA was used to analyze the differences among the types of fibers that were tested (no silane, MPTMS, and MDTMS) and the different conditions at which they were

Table 1
Polymer–fiber interfacial shear strengths (τ). SD = Standard deviation; N = number of specimens; MPTMS = 3-methacryloxypropyltrimethoxysilane; MDTMS = 10-methacryloxydecyltrimethoxysilane. Note: All values designated with A's or B's are not significantly different from all other A's or B's, respectively. Values designated with A's are significantly different from values designated with B's. The only exception is the MDTMS value in (c), probably due to the small specimen sizes. Because of this specimen size, the MDTMS value (designated with A* in (c)) is not significantly different from the NONE value in (b) and the MPTMS value and NONE value in (c)

Silane agent	Fiber conditioning	Mean τ in MPa (SD)	Min τ	Max τ	N
(a) Control specimens					
MPTMS	Control; air at 23°C	33.8 (10.1)[A]	20.5	48.0	8
MDTMS	Control; air at 23°C	33.7 (8.9)[A]	18.3	48.6	9
NONE	Control; air at 23°C	15.3 (4.2)[B]	6.8	20.2	10
(b) When fiber surface is exposed to water before droplet is applied and the specimen is tested					
MPTMS	Exposed to 60°C water	15.8 (4.8)[B]	8.6	22.6	9
MDTMS	Exposed to 60°C water	31.8 (7.7)[A]	25.0	47.1	9
NONE	Exposed to 60°C water	17.5 (4.9)[B]	10.9	23.0	7
(c) When resin was bonded to fiber then entire specimen was exposed to water then tested					
MPTMS	Exposed to 60°C water	17.6 (2.8)[B]	14.8	22.1	5
MDTMS	Exposed to 60°C water	30.5 (4.7)[A*]	26.4	36.6	3
NONE	Exposed to 60°C water	19.0 (5.9)[B]	15.7	29.5	5

tested (control–air at 23°C; silanized fibers before resin bonding in water at 60°C; and silanized fibers after resin bonding in water at 60°C) and the interaction between the two at a significance level of ($p \leq 0.05$). Results are shown in Table 1(a)–(c) indicating the subgroups that were significantly different from the others. The Tukey–Kramer procedure was used for the multiple comparisons because it controls the experiment-wise error rate ($< = 0.05$ for all pairwise comparisons, simultaneously) and can be used with unbalanced data [12].

In addition to the mechanical test results, analyses of the fiber surfaces by FT–IR microscopy were performed. Fig. 2 displays the transmission spectra of a representative: (a) unsilanized fiber, (b) a fiber coated with MPTMS and (c)

a fiber coated with MDTMS. The undulating baseline is a result of interference of the infrared radiation in the fiber, and this baseline shape varies from fiber to fiber and with sampling sites on the same fiber. Any peaks below 1550 cm^{-1} that are present in the silane are masked by the strong absorption of the E-glass. Therefore, the region used for analysis is 4000–1600 cm^{-1}. The peaks that are attributable to the silanes are at 2920 and 2854 cm^{-1} (-CH stretch) and 1730 cm^{-1} (-C = O stretch). The relative amounts of the MPTMS and MDTMS on the fibers can be qualitatively compared by their intensities provided in Fig. 2. The curves are not on an absolute scale: some have been expanded for visual purposes. From these spectra, and from the difference in absorbance under the curves (ΔA), it is evident that there is much more MDTMS on the fiber than MPTMS. Again, this difference could be caused by the difference in solubilities of silane derived products during silanization between MPTMS and MDTMS. This trend was confirmed using a number of different samples, and from a visual comparison of the fibers with the microscope. The absorbance uncertainty was taken as the root-mean-square of the variation in the baseline absorbance value from 9600 to 9400 cm^{-1} and has a value of 0.0003 absorbance units.

Fig. 3 shows transmission spectra of two microbond test samples. Prior to microscopic examination of all unexposed samples, the microbond samples were washed with acetone to remove the layer of air-inhibited resin on the outside of the droplet. The surface treatment of the samples in this figure is MDTMS. Spectra (a) and (c) are of the failure zone from the microbond test. The failure zone was identified from visual inspection to be a length directly above the sheared droplet, and the length of the zone was taken as half of the droplet diameter. Spectra (b) and (d) are from representative lengths along the fiber not in the failure zone. Spectra (a) and (b) are from the same microbond sample; spectra (c) and (d) are from a different microbond sample. It
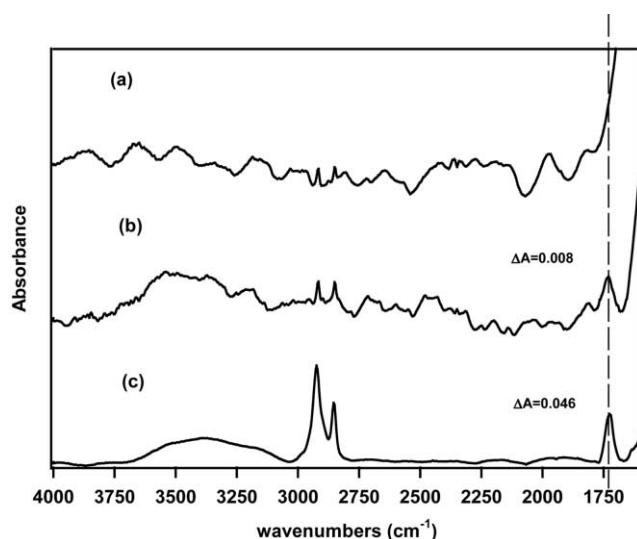

Fig. 2. FTIR transmission spectra of an unsilanized E-glass fiber (a), an E-glass fiber coated with MPTMS (b) and an E-glass fiber coated with MDTMS (c). The absorbance axis is relative, not absolute. ΔA refers to the area under the carbonyl peak.
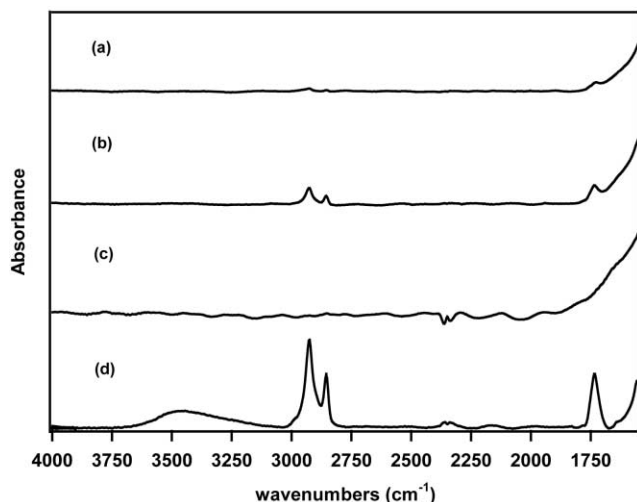
Fig. 3. FTIR transmission spectra of two microbond test samples with MDTMS. Spectra (a) and (c) are of the failure zone (the area where the droplet has been sheared from the fiber) from microbond test samples. Spectra (b) and (d) are from representative lengths along the fiber not in the failure zone. Spectra (a) and (b) are from the same microbond sample; spectra (c) and (d) are from a different microbond sample.
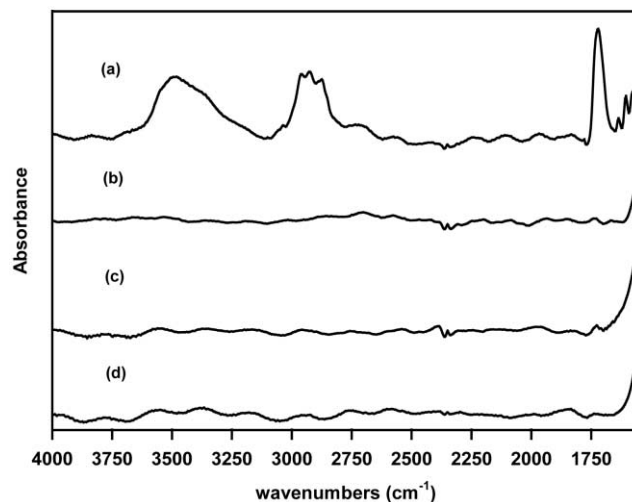

Fig. 4. (a) is a transmission infrared spectrum of the failure zone and (b) is a representative area on another part of the fiber; (c) and (d) are of the same type as (a) and (b), except of a different microbond sample. The surface treatment of the samples in this figure is MPTMS.
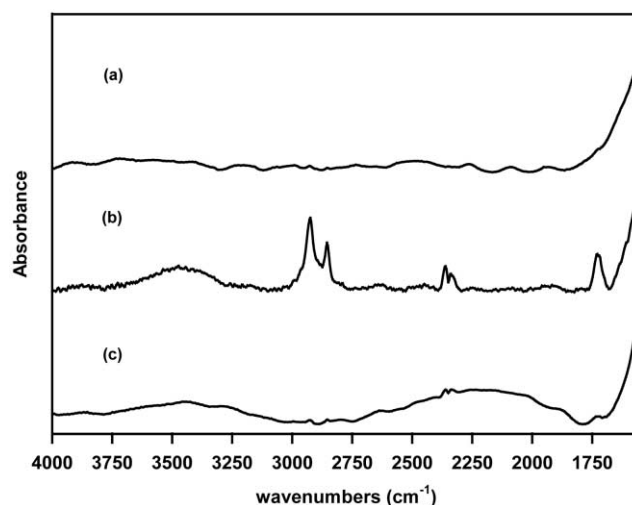

Fig. 5. Displays transmission IR spectra of the failure zone in the microbond test for three different polymer-fiber samples exposed to water at 60°C for 24 h. The surface treatment of the samples in this figure is MDTMS.

should be noted that the sampling length was the same for the failure zone and for the representative part of the fiber so that qualitative comparisons would be valid. It is quite clear from these results that the MDTMS is better adhered to the matrix than to the fiber because there is more silane in spectra (b) and (d) than in spectra (a) and (c) from comparison of the peak intensities.

The spectra of the fiber coated with MPTMS in Fig. 4 are more difficult to characterize. Like Fig. 3, Fig. 4(a) is a transmission infrared spectrum of the failure zone, and Fig. 4(b) is a representative area on another part of the fiber. Fig. 4(c) and (d) are of the same type as (a) and (b), except for a different microbond sample. Fig. 4(a) suggests the presence of the resin at the failure zone. The interfacial zone in spectra (c) is quite clean when compared to (a). Unlike Fig. 3, it is difficult to determine whether there is a difference between the amount of silane remaining at the debonded interface and on the rest of the fiber. Fig. 5 displays transmission IR spectra of the failure zone in the microbond test for specimens exposed to water at 60°C for 24 h. In two of the specimens, little or no MDTMS is present. The sample in Fig. 5(b) shows silane still present at the fiber surface. In all three samples, interfacial failure is observed. However, the failure mechanism is quite different when the failure zones for MPTMS were analyzed spectroscopically. Fig. 6(a) is a transmission spectrum of the resin. Although the silanes and the resin have many peaks that appear in the same region, a couple of peaks can be used as markers to indicate the presence of the resin: 1609 and 2966 cm^{-1}. Fig. 6(b) and (c) display the failed zone of the exposed fiber with MPTMS. According to the IR spectra, failure occurred in the matrix.

4. Discussion

These results appear to confirm our hypothesis that the longer hydrocarbon chain silane, MDTMS, with its greater hydrophobicity should offer enhanced protection of the interface to aqueous challenges compared to the shorter hydrocarbon chain and less hydrophobic silane, MPTMS. The solubility in the silanization solvent system of the dimers, trimers and oligomers derived from MPTMS is probably greater than the solubility of similar products derived from MDTMS. Therefore, the total net mass deposition onto the glass fiber would be greater for MDTMS than for MPTMS. This difference in mass deposition could be a factor in our results. One point that needs further
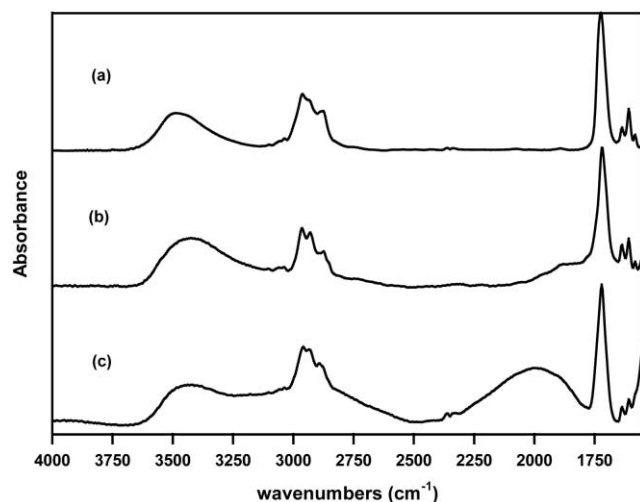
Fig. 6. (a) is a transmission spectrum of the resin. Although the silanes and the resin have many peaks that appear in the same region, a couple of peaks can be used as markers to indicate the presence of the resin: 1609 and 2966 cm^{-1}; (b) and (c) display the failed zone of the exposed fiber with MPTMS.

examination is to see if the MDTMS silanized specimens still showed enhanced resistance to degradation when the deposited silane is equal in mass to that of the deposited MPTMS. A recent study compared the coupling efficacy of equivalent amounts of MPTMS and MDTMS deposited on particulate fillers by a silanization method that employed cyclohexane and n-propylamine as the solvent and catalyst, respectively. Trends similar to ours with respect to composite durability were found [13]. Another issue that would need further exploration would be the effect of the method adopted for the application of the silane. If the method used resulted in a physisorbed silane coating instead of a chemisorbed silane coating, then there could be a significant effect on the durability of the bond [14,15]. It is encouraging that the MBT method seems sensitive enough to detect differences in the degradation behavior of the interfacial systems studied.

Another point that needs further examination is the effect of temperature per se on interfacial properties. For example, it would be instructive to compare the interfacial strength of both unconditioned and conditioned specimens at several temperatures (e.g., 37°C, 60°C and 90°C). This type of study may aid in better elucidating the causes of interfacial degradation. Previous work in this laboratory examining the stability of the interface between an epoxy resin and an epoxy-sized E-glass fiber when exposed to temperature and humidity showed no degradation of the interface after exposure to 75°C at 20% relative humidity for 1632 h [9]. This may suggest minimal impact of temperature alone, but a follow-up test should be done to assess the thermal effects on the bond strength of the resin-silane systems tested in this study. A final note on the determination of the shear strength is that values of the standard deviations that appear in the tables are larger than the standard uncertainty for the test

methodology used for this study. This indicates that the variations we are observing are indeed attributable to variations in the specimens themselves.

Transmission FT–IR microscopy was able to distinguish the silane coupling agents MPTMS and MDTMS from the resin in the interfacial region of the microbond test samples. Qualitative comparison of the carbonyl peaks demonstrates that the MDTMS produces a much thicker coating than the MPTMS under the same deposition conditions. From the FT–IR results from the samples under dry conditions, the silane coupling agent MDTMS interacted better with the matrix than with the fiber as evident by the removal of the MDTMS upon debonding of the resin droplet. This seems to suggest that factors such as the solubility parameters of the silane agent and the resin may affect the mechanism of interfacial failure. We were not able to draw analogous conclusions about the MPTMS system because of the very low intensity of the MPTMS peaks. However, the MPTMS samples exposed to 60°C water for 24 h exhibited predominantly failure in the matrix. By contrast, results were varied for the MDTMS system exposed to water for 24 h. The MDTMS was no longer present on the glass fiber for two of the specimens but was present in an appreciable quantity in the case of the third specimen.

5. Conclusions

After 24 h storage in air at 23°C, the interfacial shear strengths of polymerized resin fiber specimens silanized with either MPTMS or MDTMS were essentially the same but significantly different compared to control specimens (unsilanized fibers). However, the MDTMS silanized resin-fiber specimens showed little degradation of interfacial shear strength after accelerated aqueous exposure. This suggests that hydrophobic silane coupling agents such as MDTMS can enhance the clinical service life of dental composites. Finally, it was demonstrated that the microbond test has the potential for assessing the efficacy of coupling agents for mediating the bonding of dental polymers to glass, and also for providing a facile durability test of interfaces. The knowledge provided by this single fiber technique, coupled with the information from infrared spectroscopy and other surface analytical methods, should aid in elucidating the mechanisms of interfacial failure and thereby accelerate the development of improved dental composites.

Institute of Standards and Technology or the National Institutes of Health nor does it imply that the materials or instruments are necessarily the best available for this purpose.

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