Glass-fiber/resin interfacial strength: the microbond test and chemical evaluation

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Our aims for this paper are two-fold. First, we discuss the use of a mechanical strength test, the microbond test, coupled with chemical evaluation through the use of Fourier-Transform Infrared spectroscopy to assess changes in the strength and stability of the interface between silane coupling agents and glass fibers and between dental polymers and silanized glass fibers. We extended this work by modifying the test method so that it could be used to study adhesion to flat substrates. As a consequence, we developed a microshear test to evaluate the bond strength between dental restoratives and dental substrates such as enamel and dentin. A brief discussion of the salient features of the microshear test is included. Our second aim was to summarize the literature of bond testing and general problems of interfacial bond strength tests used by the dental research community. We conclude with the idea of holding a workshop to address the problems of bond strength testing.

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 motivation 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 (Bowen, 1962, 1963, 1964, Glenn, 1982, Draughn *et al.*, 1985, Antonucci, 1986). For silica or ceramic-reinforced polymeric composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler phase 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 (Chawla, 1987). There is a need for appropriate methods to assess changes in the strength and stability of the interface because of its important role in influencing 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 to the hydrolytically vulnerable silane-glass bond that unites the polymer matrix phase to a mineral filler phase via a poorly understood interphase. It is important to increase our understanding of this critical interfacial region so that appropriate strategies can be developed to enhance composite performance and durability by providing a better quality interface/interphase.

The Microbond Test

One such method to assess changes in the strength and stability of the interface between silane and glass is the microbond test (MBT) (Figure 1). In this test, a droplet of resin is placed on a single glass filament, embedding a length of approximately 150 µm to 200 µm. After polymerization, the polymerized droplet is mechanically sheared from the fiber, and the interfacial shear strength is then calculated by dividing the force to debond the droplet by the area of contact between the droplet and the fiber (Miller *et al.*, 1987). One potential problem of using the MBT to assess the bond strength between glass fibers and thermoset resins was the large surface to volume ratio of the droplet. This could cause a problem if highly volatile curing agents and monomers are used or if the polymerization process is severely affected by oxygen inhibition. It turned out that, due to the relative non-volatility of the dental resins and photoinitiators and the rapidity of the light curing process, we found the light-cured dental resins to be ideal resins for this test method. By means of the MBT, a wide spectrum of resin systems, coupling agents and glass or ceramic fibers can be screened for use in dental composites. 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.

Past Research

Materials

To illustrate this point, the MBT was used to assess the efficacy of two chemically different silane coupling agents, 3-methacryloxypropyltrimethoxysilane (MPTMS) and 10-methacryloxydecyltrimethoxysilane (MDTMS), before and after aqueous challenge. We also examined whether the longer hydrocarbon chain [$-(CH_2)_{10}-$] silane, MDTMS, with its greater hydrophobicity, offered enhanced protection of the interface to aqueous challenges compared to the shorter, less hydrophobic [$-(CH_2)_3-$]silane, MPTMS. The details of this work can be found in (McDonough *et al.*, 2001).

The monomers 2,2-bis [p-(2'-hydroxy-3'-methacryloxypropoxyphenyl)]propane, (Bis-GMA), and triethylene glycol dimethacrylate, (TEGDMA) were used to prepare the resin. The resin was photo-activated by the addition of the photo-oxidant, camphorquinone and the photo-reductant, ethyl 4-N,N-dimethylaminobenzoate, 4EDMAB. The composition in mass fraction of the photoactive resin was: Bis-GMA: 0.695, TEGDMA: 0.295, CQ: 0.002, and 4EDMAB: 0.008.

Results and Discussion

Mechanical testing

As can be seen in Table 1, although the MPTMS and MDTMS silanized fibers coupled well initially to polymerized droplets and gave similar mean bond strength (τ) values, only those fibers coated with MDTMS retained their strength when the specimens were exposed to moisture. 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 potential difference in mass deposition could have been a factor in our results.

Surface Analysis

In addition to the mechanical test results, we analyzed the failure surfaces on the fibers by using Fourier Transform Infrared (FT-IR) spectroscopy. Figure 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 caused by 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 was from 4000 cm^{-1} to 1600 cm^{-1}. The peaks that are attributable to the silanes appear at 2920 cm^{-1} 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 Figure 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 carbonyl peaks of the curves (ΔA), there appears to be more MDTMS on the fiber than MPTMS. Again, this difference could be caused by the difference in solubilities of silane-derived products not crosslinked or attached to MPTMS and MDTMS and the resulting difference in mass of silane deposited. This trend was confirmed using a number of different samples and from a visual comparison of the fibers with the microscope, but more analysis would be needed to quantitate the findings.

Figure 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 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.

The spectra of the fibers coated with MPTMS is shown in Figure 4. Like Figure 3, Figure 4 (a) is a transmission infrared spectrum of the failure zone, and Figure 4 (b) is a representative area on another part of the fiber. Figures 4 (c) and (d) are of the same type as (a) and (b), but from a different microbond sample. Figure 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).

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 indicated that the MDTMS produced a much thicker coating than the MPTMS under the same deposition conditions. FT-IR results from the samples under dry conditions showed that 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 ^{o}C water for 24 h showed mostly 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.

After 24 h storage in air at 23 ^{o}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 about silane-derived interfaces 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. Recently, Debnath *et al.* (2003) used this test to determine silane treatment effects on glass/resin interfacial shear strengths. They found a positive correlation between the amount of silane on the filler surface and the property loss after soaking.

In other work using the microbond test, Antonucci *et al.* (1995) ran a 2 x 3 factorial design test investigating silanized and unsilanized E-glass fibers and three visible light-activated resins: Bis-GMA/TEGDMA, UDMA (a diurethane dimethacrylate derived from HEMA and 2,4,4-trimethylhexane-1,6-diisocyanate), and FUDMA (a flexible poly(ethylene glycol) derived diurethane dimethacrylate that forms an elastomeric crosslinked polymer.) For both silanized and unsilanized fibers, UDMA showed the highest bond strength and FUDMA showed the lowest bond strengths.

Microshear test

We extended the work on the microbond test of polymer-glass systems to other dental substrates by developing the microshear test so that it could be used with flat substrates (McDonough *et al.*, 2002). Similar to the microtensile test, the microshear test calls for bonding many specimens on a flat substrate such as dentin or enamel. Advantages of the microshear test are that it allows for both the regional mapping of the mineralized surface and aid in the conservation of extracted teeth needed to provide the relevant substrates for bonding studies. Part of this work addressed concerns about shear testing in general. By using finite element analysis, we showed that while it was possible to maximize the shear load that can be applied, there will always be a strong tensile component. Should the bond strength be significantly weaker in tension than in shear, then the tensile failure mode would overwhelm any design attempts to induce the specimen to fail in shear. Future work will include FT-IR microspectroscopy mapping of the surface of the debonded areas of the specimens to determine the mode of failure (Schumacher *et al.* 2001, Tesch *et al.*, 2001). FT-IR examination can identify areas of adhesive resin, dental restorative composite and dentin in the failure zone. From this analysis, the researchers hope to identify critical elements in the fracture pattern that may elucidate bond failure mechanisms.

Assessment of bond strength measurement in dental research

Measuring bond strengths, regardless of the technique chosen, is a very controversial topic not only in dental adhesion, but also to the general area of adhesion testing. We were asked by the organizers of this meeting to give a brief assessment of measuring bond strengths in the dental community. That subject, in and of itself, would make for a full paper. Thus, we have chosen to touch upon some of the major points of contention in this field and to talk about possible ideas to address these issues.

General comments

To determine the real efficacy and durability of polymeric dental adhesives, thorough clinical testing is necessary. However, in practice, long term clinical testing is expensive and commercial adhesive materials are constantly undergoing changes so that the clinical testing necessary to evaluate their long-term properties and success rates becomes impractical. Adding to this challenge are the very complex conditions that an *in vivo* tooth cavity preparation presents to achieve effective adhesion of the restorative material to enamel and dentin. The mineralized tissues comprising tooth structure, enamel with its prismatic, rod-like apatitic morphology, and dentin with its array of dentin tubules, are complex, anisotropic materials. This anisotropy in the case of the highly mineralized enamel is largely related to the orientation of the enamel rods. Dentin anisotropy is a result of structural changes where fibrillar collagen interdispersed with a crystalline apatitic mineral also exhibits tubular variation and decreased intertubular dentin, especially with increasing depth away from the tooth surface toward the pulp. Dentin thus presents a more complex substrate than enamel for bonding. In addition, the polymeric adhesive restorative is a viscoelastic material that, in the hostile oral environments, is exposed not only to mechanical and physical forces, but also a constant onslaught of biological and chemical challenges, as well as cyclic exposure to heat and cold. This list of *in vivo* factors that can affect adhesion to tooth structure is not meant to be exhaustive, but rather, illustrates the complex nature of properly assessing the bond between the restorative and the variable mineralized tooth structure, and points to the challenges involved in designing a reliable in vitro screening test for assessing adhesion.

Measuring bond strengths between dental substrates and dental restoratives is a very complex and, at times, even emotional issue. At present there are many techniques that researchers use to measure bond strength, and just as many different techniques are used, many different testing conditions are used for each test – there are no standards. As such, inter-laboratory comparisons of data are tenuous at best and practically impossible. Stanley (1993) made a plea for a standardized bonding test. He pointed out the questionable clinical relevance of *in vitro* test results. He criticized the lack of experimental detail that might have permitted him to assess the value of the *in vitro* results in a number of papers presented at the International Association of Dental Research (IADR) 71st General Session. Descriptions of the experimental conditions were either non-existent, or varied greatly even when the same test was being conducted. He stated that “such a variety of so-called ‘scientific’ testing accumulates a hodgepodge of data that can present very misleading conclusions that may be totally unrelated to clinical relevance.” He goes on to say that investigators “…boastfully present statistically significant results. But what is this worth when the substrate (dentin) used is such an unknown quality and so many factors are ignored? The establishment of a uniform dentin substrate must be the number one priority.” He points out that although the International Organization for Standardization (ISO) is working on a draft to standardize an *in vitro* method, he did not know its relevance to *in vivo* testing. These concerns were published in 1993, yet a recent search of the Science Citation Index shows only 12 citations of Stanley’s comments. As of 2003, we still do not have a standardized test or procedure to systematically measure bond strength.

Standardization of test methods

A technical specification for a testing standard is being developed by the ISO. The authors of the standard acknowledge that while bond strengths cannot predict exact clinical behavior, they may be useful for batch quality control. On the one hand, one can see the value of having standard test procedures to help in comparing results from different laboratories. On the other hand, the nature of the dentin substrate may preclude meaningful comparisons. When these bond tests are used, the numbers generated would seem to be more indicative of the ability to make the sample than they are of any material property. Rich *et al.* (2002) discuss the work involved in a round robin assessment of the single fiber fragmentation test, a test commonly used to measure fiber-matrix interactions. Interestingly, their paper describes a recent retest where the specimens were made by one laboratory and distributed to all participating laboratories. Using a standard testing procedure, consistent results were obtained among the laboratories.

Now let us look at some of the comments in the literature on different test methods:

Shear bond testing

Rasmussen (1978) noted that there were no widely accepted tests for measuring bond strengths in dentistry. In his review, he found that existing bond-strength testing methods are sensitive to the alignment of load, that bond strength measurements are dependent upon film thickness, the stress calculated from the breaking load and the fractured area is not the actual stress resulting in failure, bond tests are designed for study in air at room temperature rather that environments simulating oral conditions, and finally, that since the greatest stress is not necessarily at the bond interface, cohesive failure does not directly imply that the adhesive bond is stronger than the material in which the failure occurred.

Van Noort *et al.* (1989) examined the validity of the currently accepted method of measuring bond strength. Using finite element techniques, the authors demonstrated that tensile and shear bond strength tests are highly dependent on the geometry of the test arrangement and that the convention of dividing the failure load by the bond area does not stand up to close examination. For shear loading, they showed that the interfacial tensile/compressive stresses increase as the distance between the point of load application and the dentin surface is increased. They found high tensile stresses to be generated at the bond line and found that they invariably overshadowed the shear and peel stresses at the interface. The authors also found that results of tests to determine the bond strength between dental materials and tooth tissues are so severely affected by the test conditions that comparisons of data from different laboratories are probably impossible. Even for similar tests performed in the same laboratory large variations can arise. This is particularly so for the shear tests if the point of load application is not very carefully controlled. The bond strengths can only be used for a comparison of the effectiveness of bonding agents, and cannot be related directly to what might happen clinically. Ultimately, they argued for the need to standardize test procedures used to measure bond strengths so that a universally valid comparison between different bonding agents can be made.

DeHoff *et al.* (1995) concluded that no evidence has yet shown that bond strength is relevant to clinical performance and that a critical factor in assessing the usefulness of bond tests is a thorough understanding of the stress states that cause failure in the bond test and then to assess whether these stress states also exist in the clinical situation. They further stated that published bond strength data on the same systems showed great variability in mean bond strength values with large standard deviations. They found it highly unlikely that mechanical bond strength tests will ever yield data that define bond strengths as unique values for a given bonding system. Thus, these tests should be used only as screening tests to compare one system with another using the same test configuration. Calculated stress states in the shear bond test indicate that average bond strength values determined by dividing the failure load by the total bonded area grossly underestimate the true failure stress. Also, even with standardization of testing procedures, it is likely that bond strength values will vary from laboratory to laboratory because the failure of brittle materials is highly technique sensitive. Ultimately, they believed that the prediction of service performance should be based on fracture mechanics concepts and cyclic loading parameters that account for the variability and time dependency inherent in the failure of brittle materials.

Rasmussen (1996) suggested that adhesive failure in many dental shear bond strength tests does not occur as a consequence of shear stress but as a consequence of tensile stress induced by a bending moment. He concluded that the calculation of shear bond strength is inappropriate for these test methods and that dental researchers should be measuring the stress that initiates debonding rather than average stress.

Versluis *et al.* (1997) asked why shear bond tests pull out dentin. By using numerical modeling, they confirmed that high tensile stresses initiated cracks that subsequently diverged into dentin and that dentin pull-out was partly due to the biomechanics of the shear test. They concluded that dentin pull-out during the shear test did not necessarily mean superior adhesive strength or that the cohesive strength of the dentin was reduced.

Sudsangiam and Van Noort (1999) also questioned the usefulness of dentin bond tests. They concluded that at present, clinically based evidence remains the only reliable means for the selection of dentin bonding agents. They felt that a shear test may easily transform into a bend or cleavage type of test where tensile and not shear stresses dominate. They argued that no amount of standardization could overcome inconsistency problems if a test is fundamentally flawed, and they felt that the shear test is such a test. They stated that the popularity of the shear test could be explained by its relative simplicity to perform, but that this reason is not a good reason for its continued use. They preferred using the microtensile test and the fracture mechanics approach in improving the understanding of the properties of the adhesives interface. Despite this, they concluded that the acceptance of these approaches by the wider research community will probably be poor because these approaches are much more difficult to do. They felt that the most popular methods to evaluate bond strengths to enamel and dentin clearly bear no relationship to the clinical situation. Bond strength values depend on the method used, should be carefully interpreted, and comparison of the results from different laboratories is not possible. They concluded that, in terms of new information it can provide, the shear bond strength test should not be used.

Recently, Dickens and Milos (2002) examined the relationship of dentin bond strengths to different laboratory test designs. They felt that since the shear bond test will remain a favorite among researchers, the variability in the reported results supports the need for standardization of a bond test to allow data screening and comparison between laboratories and that no clinical inferences should be made on such evaluation. Unless a generally accepted standard is in place, the chisel-on-iris technique, although not entirely free of inherent problems, is preferred over the other tests that they examined, as it avoids obvious extraneously introduced failure modes. Although they acknowledge that some flash outside the iris opening may have contributed to the higher values, they point out that using an iris provides a distributed load over a 180° half circle.

Tantbirojn *et al.* (2000) addressed the problems inherent in the conventional shear test by comparing the performances of six dentin bonding agents subjected to an interfacial fracture toughness test and the shear bond test . The study suggested that the results obtained from the interfacial fracture toughness test were only marginally different from those obtained by the nominal shear test. They expressed concern, however, that shear test may not be able to estimate bond strengths if future generations of bonding systems get appreciably better. For the shear bond test, if dentin pull-out was observed in the failure surface, then the calculated nominal bond strength was no longer based on the cross-sectional area. Thus, they concluded that the bond test could not discriminate between good and very good bonding agents.

Holtan *et al.* (1994) noted that in attempting to improve bond strength of dentinal adhesives, manufacturers and their researchers face some formidable obstacles. Dentin is a living tissue that consists of inorganic compounds, organic compounds and water. When dentin is mechanically prepared for bonding, a smear layer is formed that is superficially attached to the intact dentinal surface. In their work using the shear test, they found that most of the specimens failed within the resin composite or the dentin itself, but not at the dentin/adhesive resin interface. The authors further noted that, in addition to continually trying to improve bond strengths, the manufacturers also have to avoid making the actual restorative process too complex or time consuming. This is clinically relevant because materials advance not only in terms of property improvement but also by controlling chairside difficulties.

Perdigao and Lopes (1999) reviewed the most recent concepts in dentin bonding. They concluded that although the utility of laboratory bond strength studies is doubtful as far as clinical performance is concerned, bond strength studies are still necessary in order to compare similar parameters among materials.

Assessment of shear bond testing

We see some clear trends. One trend is to criticize the shear tests and to point out its many flaws. Another trend is that the shear tests, in all its permutations, continues to be used by the dental community along with other test methods. Although the users of the shear techniques acknowledge the limitations and criticisms of the technique, they use it for screening and inter-material comparisons. The shear tests are considered to be easier to run than microtensile tests and seem to give essentially the same trends as that achieved by using the microtensile test. That being said, the shear tests are not true shear tests. Van Noort *et al.* (1989), DeHoff *et al.* (1995), Rasmussen (1996) and McDonough *et al.* (2002) pointed out in their work that there are large tensile loads that are imparted in most shear tests. Packham (1992) notes that in conventional shear tests there is considerable nonuniformity of stress throughout the joint. He described a napkin ring test wherein the variations in the shear stress state were minimal. It consists of two thin-walled tubes joined end to end by a thin layer of adhesive. The torque required to break the joint is recorded. Despite relative uniformity of stress, some stress concentration may occur at the edges of the adhesive. In another field of research, Pocius (1998) writes about the lap shear test commonly used in the adhesives industry: the D1002 lap shear test is much maligned. He observes that the combination of shear load and normal loading of the adhesive forms the basis for the major criticism of this specimen. Despite the stress state and lack of realism, the lap shear specimen has been used to evaluate essentially every adhesive. Because of its simplicity, this specimen will likely continue to be used extensively in the evaluation of adhesives. This conclusion seems to have been reached by the critics of shear testing in dental applications as well.

Tensile Testing

Sano *et al.* (1994) introduced the microtensile bond test to the dental community. The main findings of their study were that the tensile bond strength is dependent upon the bonded surface area and that cohesive fractures of dentin are not seen clinically with dentin adhesive restorations. Readers who are interested in a thorough review of the microtensile test are directed to Pashley *et al.* (1999). They note that the microtensile test methods offer versatility that cannot be achieved by conventional methods. It is more labor-intensive than conventional testing, but holds great potential for providing insight into the strength of adhesion of restorative materials to clinically relevant sites and substrates. They point out that as bonding techniques and materials improved, the bond strengths became high enough to cause cohesive failures in dentin when using conventional shear and tensile tests, i.e., dentin broke from dentin, leaving the resin-dentin interface intact. Such failures of the substrate preclude measurement of interfacial bond strengths and limit further improvements in bonding formulations, since the tests can no longer detect improved adhesion. The purpose of the review was to describe all of the various modifications of the microtensile test in one paper so that investigators can select the modification that best suits their testing needs.

One claim in the early microtensile papers was that of mostly adhesive failure surfaces. Armstrong *et al.* (1998) used the microtensile test and found, unlike earlier reported work, that cohesive fractures of either dentin or composite accounted for 55 % of the total failure modes. They concluded that the versatile new method permits multiple measurements from a single tooth or small surface areas within a restoration but careful interpretation of the failure mode is required to prevent inappropriate conclusions about the utility of the test. Pocius (1998) writes that:

> “The mode of failure means the locus in the adhesive bond through which failure propagates. If we can visually see adhesive on both sides of the specimen, we use the term ‘failure in cohesion.’ If we visually inspect the adhesive bond and find what appears to be adhesive on one adherend and

> adherend surface on the other adherend, we describe the failure as 'apparent failure in adhesion.' Note that the word 'apparent' is used. Failures that are visually in adhesion may not necessarily be failures in adhesion. A thin cohesive failure near the adherend surface could have occurred. Such a failure can be detected by modern surface analysis techniques or proper application of older techniques such as staining or contact angle measurements. Sophisticated users of adhesives not only specify the strength of an adhesive used in a certain bonding situation but also specify the mode of failure that is observed when that bond is tested."

Nakabayashi *et al.* (1998) determined the efficacy of a miniaturized dumbbell test procedure designed to more easily identify defects in bonded dentine specimens. Cohesive failure in the bonding resin was observed. They agreed with other investigators that traditional shear strength tests are misleading because the knife edge used delivers non-uniform stress distributions to the resin and crack propagation often proceeds unimpeded through the resin or dentin rather than through the interface between the resin and dentin. If the interfacial bond strength is to be evaluated, the stress must be delivered uniformly at the resin/dentin interface.

Schreiner *et al.* (1998) compared the microtensile and shear bond strengths of five commercial dentin adhesive systems. Fracture sites were observed using light microscopy and scanning electron microscopy to determine the type of failure involved. The shear bond test produced significantly more failures within dentin and composite than the microtensile method. They concluded that the microtensile test produced a more definitive assessment of adhesive bond strength than the shear bond test. They stated that since clinical failures result primarily from tensile forces, and because microtensile testing utilizes tensile rather than shear forces, the microtensile methodology should more closely approximate clinical applications.

Tay *et al.* (2000) used the microtensile test to see if the smear layer thickness had any effect on the bond strength of self-etching primers to dentin. They used the "non-trimmed" beam shape technique of the microtensile test. They show images where cracks originated on edges and corners. They noted that recent studies using microtensile dumbbell shaped specimens reported similar substrate failure. They felt that occurrence of cohesive substrate failures reflects the non-uniform stress distribution within the bonded assembly that is inherent in a strength-based test and cannot be attributed to the bond strength of the adhesive being greater than the ultimate tensile strength of dentin or the yield strength of resin composites.

Assessment of tensile testing

To sum up the situation for tensile testing, a growing amount of research is being done using the microtensile variation. Yet issues remain such as: How are samples that fail during specimen preparation treated? Is the test too time-consuming and labor intensive to be accepted by the dental research community? Are the results clinically relevant? If we put adhesive too close to the bond line when attaching the specimen to the grips, then are we violating Saint Venant's Principle which says that we need to grip the specimen far away from the area to be tested to minimize the effects of the grips on the testing results?

Fracture Mechanics

Fracture mechanics has a strong scientific basis and holds promise for dental materials. Rasmussen (1978) used a controlled fracture technique to study dental adhesion issues. He introduced a new parameter called the interfacial work of fracture that represents an average of the energy for initiation and propagation of a crack through the interface separating two adhering materials. One of his goals was to develop a test that would allow for the investigation of the adhesive bond alone. Mecholsky (1995a) discusses fracture mechanics principles, and in Mecholsky (1995b), he discusses the application of quantitative fracture surface analysis to basic research and product development. Ruse *et al.* (1996) describes a novel fracture toughness test that used a notchless triangular prism specimen. They felt that the commonly used chevron-notched short rod (CNSR) specimen is cumbersome and difficult to control and is prone to error when used to characterize bonded interfaces. They wanted to retain the overall geometry of the CNSR but wanted to avoid the cumbersome notching process. Armstrong *et al.* (2001) had success with both the microtensile test and the CNSR test in determining modes of failure in bonded joints.

One word of caution regarding fracture mechanics comes from Potter (1978) where he states:

> "As a result of the work of Griffith and Irwin, it is now accepted that the apparent reduction in strength is due to the presence of naturally occurring micro-cracks which give rise to high local stress concentrations. Isotropic fracture criteria are based upon the strain energy conditions under which these micro-cracks will propagate in an unstable manner. Although ductility may reduce their effect, these micro-cracks invariably act as stress concentrators and can cause only a reduction in the applied stress at fracture.
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> The great success of linear elastic fracture mechanics in predicting the behavior of isotropic material has led, almost hypnotically, to its direct application to composites with little or no modification. However, even if the micro-cracks in the damage zone are the direct result of the composite being overstressed, they do not in practice precipitate immediate failure. Indeed in some cases they appear to act as stress relievers since, although the composite may be considered linear-elastic to failure, the notched laminate fails at a stress greater than that indicated by the linear elastic stress concentration. It follows that the direct application of conventional

> fracture mechanics cannot be justified since such delayed failure cannot be explained by a micro-crack which acts as a concentrator of tensile stress."

Final comments

As we see, Stanley's complaint about the hodgepodge of data still seems to be valid. Nothing is standardized, clinical relevancy has not been established, yet bond strength testing continues unabated. How important is it to standardize these tests? Are the test results meaningful? Do we want a bond that is so strong that when failure occurs, it is in the tooth? Is there a minimum bond strength value that new materials must exceed to pass a screening test? We hear that secondary caries, through microleakage, is the main source of failure in polymeric composite restoratives. Can any of these tests predict such a failure?

Even though bond strength testing has many issues, there are some positive signs. Whether it be the work presented here on the microdrop test, work being done on the microtensile test, the fracture mechanics approaches, the use of chemical analysis and the use of numerical methods, the dental community is trying to address the issues raised in this paper. What can we do as a community to better address these issues.

One place to start may be a workshop that brings together researchers, manufacturers and clinicians. In such an environment, let those researchers who feel that these tests are meaningless make their case, and have the proponents of the tests make their defense. Let the manufacturers explain to us what they need to make their decisions. Let the people calling for standards explain how they will address the complexities of sample preparation. We may be able to develop a standard substrate and testing protocol to aid in inter-laboratory comparisons. At the very least, we can begin to respond to Stanley's plea and make bond strength testing more useful and coherent to the wider dental community. NIST has had success in running such workshops, and we refer you to the following reports: McDonough *et al.* (1997) and McDonough *et al.* (2000) to get a sense of what can be accomplished. These reports can be found at: http://polymers.msel.nist.gov.

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Table 1
Polymer-Fiber Interfacial Shear Strengths (τ)
1a Control specimens

Silane agent	Fiber Conditioning	Mean τ in MPa (SD)	Min τ	Max τ	n
MPTMS	CONTROL; AIR AT 23 ^{o}C	33.8 (10.1)^{A}	20.5	48.0	8
MDTMS	CONTROL; AIR AT 23 ^{o}C	33.7 (8.9)^{A}	18.3	48.6	9
NONE	CONTROL; AIR AT 23 ^{o}C	15.3 (4.2)^{B}	6.8	20.2	10
1b When fiber surface is exposed to water before droplet is applied and the specimen is tested					
MPTMS	EXPOSED TO 60 ^{o}C WATER	15.8 (4.8)^{B}	8.6	22.6	9
MDTMS	EXPOSED TO 60 ^{o}C WATER	31.8 (7.7)^{A}	25.0	47.1	9
NONE	EXPOSED TO 60 ^{o}C WATER	17.5 (4.9)^{B}	10.9	23.0	7
1c When resin was bonded to fiber then entire specimen was exposed to water then tested					
MPTMS	EXPOSED TO 60 ^{o}C WATER	17.6 (2.8)^{B}	14.8	22.1	5
MDTMS	EXPOSED TO 60 ^{o}C WATER	30.5 (4.7)^{A*}	26.4	36.6	3
NONE	EXPOSED TO 60 ^{o}C WATER	19.0 (5.9)^{B}	15.7	29.5	5

SD = standard deviation and is taken as an estimate of the standard uncertainty
n = number of specimens
MPTMS = 3-methacryloxypropyltrimethoxysilane
MDTMS = 10-methacryloxydecyltrimethoxysilane

Note: All values designated with As or Bs are not significantly different from all other As or Bs, respectively. Values designated with As are significantly different from values designated with Bs. The only exception is the MDTMS value in Table 1c, probably due to the small specimen sizes. Because of this specimen size, the MDTMS value (designated with A^{*} in Table 1c) is not significantly different from the “NONE” value in Table 1b and the MPTMS value and “NONE” value in Table 1c. Two way ANOVA was used to analyze the differences among the types of fibers that were tested and the different conditions at which they were tested and the interaction between the two at a significance level of ($p \leq 0.05$). Results are shown 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 (SAS Institute, 1989).

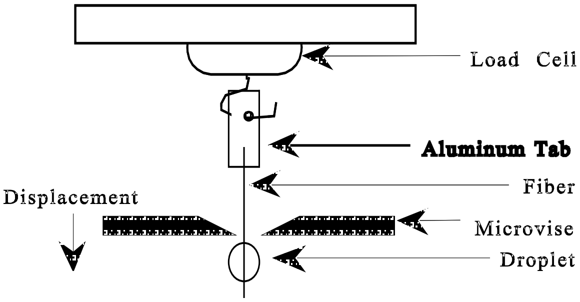

Figure 1: Schematic of Microbond Test Apparatus.

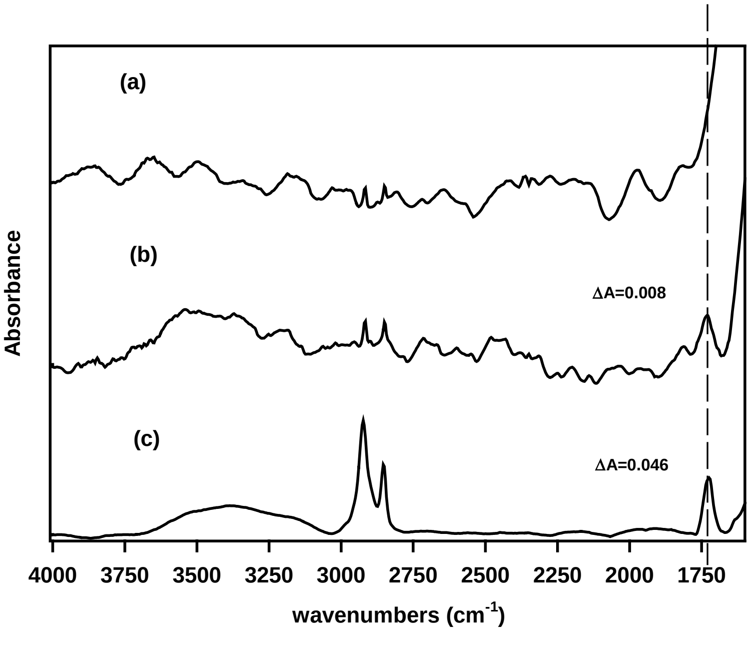

Figure 2: FTIR transmission spectra of an unsilanized E-glass fiber (a), an E-glass fiber coated with MPTMS (b), and an E-glass fiber coated with MDTMS (c). The absorbance axis is relative, not absolute. ΔA refers to the area under the carbonyl peak.

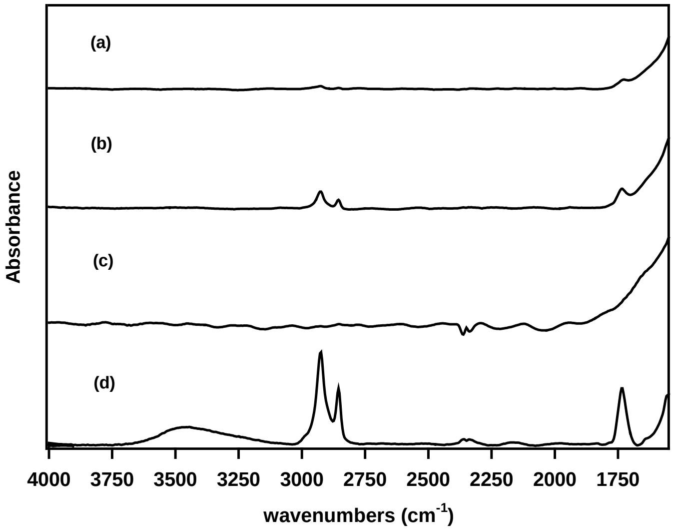

Figure 3: FTIR transmission spectra of two microbond test samples with MDTMS. Spectra (a) and (c) are of the failure zone (the area where the droplet has been sheared from the fiber) from microbond test samples. Spectra (b) and (d) are from representative lengths along the fiber not in the failure zone. Spectra (a) and (b) are from the same microbond sample; spectra (c) and (d) are from another microbond sample.

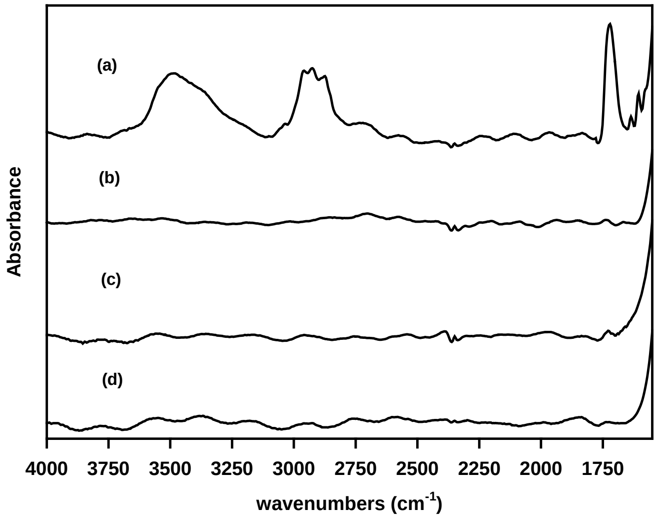

Figure 4: Figure 4 (a) is a transmission infrared spectrum of the failure zone, and Figure 4 (b) is a representative area on another part of the fiber. Figures 4 (c) and (d) are of the same type as (a) and (b), except of a different microbond sample. The surface treatment of the samples in this figure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