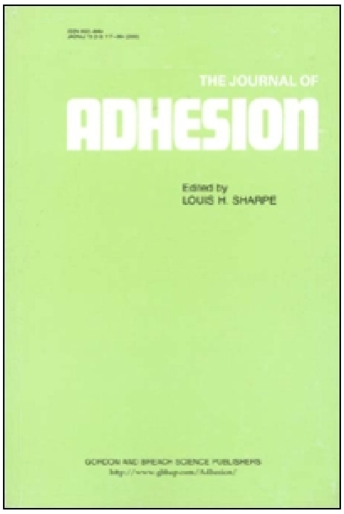

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A Direct Comparison of the Fragmentation Test and the Microbond Pull-out Test for Determining the Interfacial Shear Strength

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Experiments were conducted to compare the fragmentation test with the microbond pull-out test for determining the interfacial shear strength between carbon AS4 fibers and a thermoset matrix consisting of a Di-Glycidyl Ether of Bisphenol A (DGEBA) resin cured with a diamine (meta-phenylenediamine, m-PDA) curing agent. The results indicate that, for the microbond test, diffusion of the rather volatile m-PDA curing agent at early stages of cure leads to low values of interfacial shear strengths when compared with results obtained for the same system with the fragmentation test.

With the microbond test, a distinct relationship between the glass transition temperature of the droplets and their size is noticed. Smaller ($<150\,\mu$m) droplets have very low Tg's and are incompletely cured. While changing to a modified curing cycle and/or using a m-PDA-rich curing environment alleviates the diffusion problem, the interfacial shear strength values are still not in good agreement with the fragmentation test results. Microbond data from another system consisting of DGEBA resin cured with a different, less volatile dimaine curing agent indicates that diffusion of the curing agent becomes less severe as the volatility of the curing agent decreases and the corresponding microbond interfacial shear strengths agree better with fragmentation test results.

KEY WORDS Single fiber fragmentation test; microbond pullout test; interfacial shear strength; interface; fiber-matrix adhesion; variable stoichiometry effect on epoxy properties.

INTRODUCTION

The interface between polymer matrix and reinforcing fiber plays a key role in determining final mechanical properties of the composite material. "Good" adhesion and bonding at the interface is paramount for achieving high interfacial shear and off-axis strength. "Good" adhesion is also necessary for efficient load transfer and long term property retention. Since the interface plays a key role in transfering the stress from the matrix to the fiber, it is important to be able to

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* Corresponding author.

characterize the interface and level of adhesion to understand composite performance properly. Thus, it is essential to have reliable laboratory techniques to study fiber-matrix interfacial interactions.

Several techniques have been developed in an effort to measure the interfacial shear strength directly. In one technique, a single fiber composite sample is loaded in tension in the fiber direction until the fiber fractures into a distribution of critical length size fragments. These single fiber tests (fragmentation tests) have been used to study glass fiber/resin interactions by Frazer *et al.*,[1] carbon fiber/expoxy interactions by Drzal *et al.*[2,3] and highly cross-linked brittle systems by Lee and Holguin.[4] A second method is the single fiber pullout test. A small length of fiber is embedded in a thin disk of resin and the force needed to extract the fiber from the resin is measured and used to calculate the interfacial shear strength, τ, using the equation:

$$\tau = \frac{F}{\pi d L} \tag{1}$$

This test has also been used, with some success, to study the adhesion of thermosetting resins to glass and carbon fibers.[5,6] A limitation inherent in these types of pull-out tests is met when small fibers having diameters of 10 microns or less are used. If the pull-out force exceeds the fiber tensile strength, the fiber breaks before successful pull-out occurs. Thus, very short embedment lengths (0.04–0.05 mm) are necessary to complete these pull-out tests successfully. Such small embedment lengths are difficult to work with in practice, although some investigators have reported limited success with specially designed apparatus[7] for such tests.

Due to the problems inherent with conventional pull-out methods and with other interfacial testing methods, a new pull-out test version has been developed by Miller *et al.*,[8,9] and used by others,[10,11] which provides a more convenient method for measurement of interfacial shear strengths of fiber/resin interfaces. Because this method uses very small amounts of resin, it is commonly referred to as the microbond pullout technique or test.

This study was undertaken to examine the microbond technique as it applies to determination of interfacial shear strengths of carbon fibers (AS4) with thermoset matrices (epoxy) as well as to compare it with the fragmentation test described earlier.

EXPERIMENTAL

I. Materials

Carbon fibers (AS4, Hercules, diameter 7.78 microns) were used throughout this study. A diglycidyl ether of bisphenol A (DGEBA) (Epon 828, Shell) was used as the model epoxy resin. The two curing agents used in this study were both di-amines. Meta-Phenylenediamine (m-PDA) was used as the baseline curing agent. The other curing agent used was Jeffamine-700 (Texaco) (a liquid, viscous polyetheramine curing agent containing oxypropylene units between the amines). The number following the trade name represents the approximate average molecular weight of the curing agent. A stoichiometric amount of curing agent was used in all cases except where noted. Three different curing cycles were used in this study: (1) a "normal" curing cycle (abbreviated "NCC"-75°C-2 HR, 125°C-2 HR), (2) a "modified" curing cycle (Room Temperature-24 or 36 HR, 75°C-2 HR, 125°C-2 HR) and (3) a curing cycle for the J-700 curing agent which is listed in Table II.

II. Microbond pull-out technique

The procedure used to fabricate samples for the microbond test is very similar to that described by Miller *et al.*[8] with a few modifications. It involves deposition of a small amount of resin on to the clean surface of a fiber in the form of several microdroplets. The droplets form concentrically around the fiber in the shape of ellipsoids and retain their shape after appropriate curing. Once cured, the microdroplet dimensions and fiber diameter are measured with the aid of an optical microscope. The embedded length is fixed by the diameter of the microdroplet along the fiber axis, which is dependent on the amount of resin deposited on the fiber. In these experiments, 6″ (15 cm) lengths of fibers were stretched across a rectangular frame and held in tension while random droplets of various sizes were deposited on the fibers with the aid of a very thin (30 guage) needle; this fiber collection was then appropriately cured. The practical minimum limit for embedment length using this technique is about 70 microns. An example of a typical microdroplet is shown in Figure 1.

In this work, a fiber holder and straining device, mounted horizontally and positioned under an optical microscope, was used to collect the data. One end of the fiber specimen is fixed with adhesive to a metal tab which is connected to a loadcell (the microdroplets are sheared off the fiber at a rate of about 0.1 mm/min using a moveable stage). To grip the droplet, an adjustable micrometer equipped with flat, rectangular cross-section blades is used. The blades of the micrometer are first positioned on one side of the droplet, then the blades are brought into contact with the fiber and then opened slightly to let the fiber, but not the droplet, move between them. The moveable stage is used to translate the fiber and droplet laterally in the horizontal plane. As the blades continue to move, they make full contact with the droplet and an axial force detected by the loadcell is exerted on the droplet. The axial force on the droplet is then transferred to the fiber through a shearing force at the fiber/matrix interface. When the shearing force exceeds the interfacial bond strength, detachment occurs, and the droplet is displaced horizontally along the axis of the fiber. The maximum in the force curve is taken as the point at which the droplet has debonded from the fiber. A schematic of the experimental pull-out apparatus is shown in Figure 2.

In practice, about 8 microdroplets are deposited on each fiber specimen, each

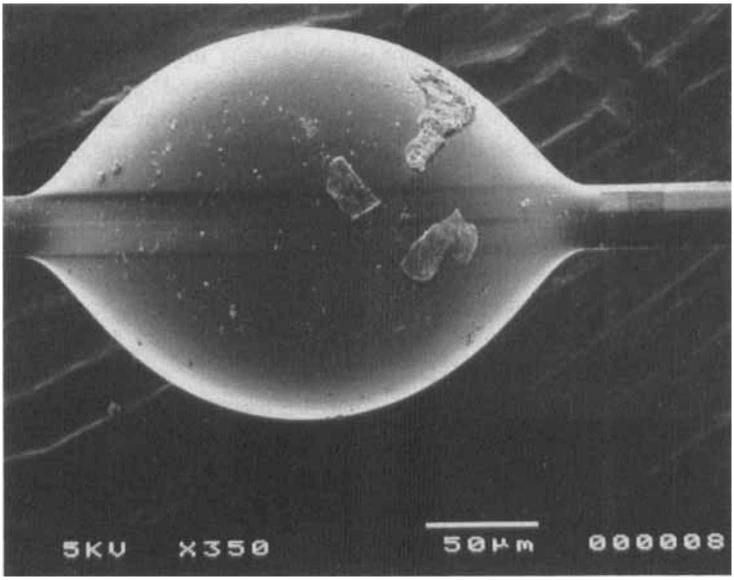

FIGURE 1 SEM Micrograph of a typical droplet on a polyethylene fiber with diameter = 28 microns.

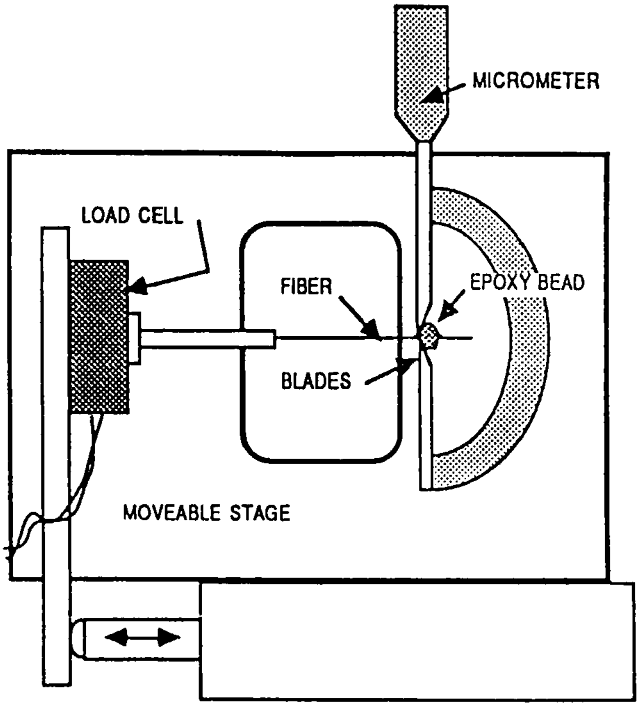

FIGURE 2 Droplet Pull-Off Test Apparatus.

about 10 mm apart. After each droplet has been tested in this microbond process, the blades are opened and the stage and sample are positioned to the next droplet.

III Single fiber fragmentation test

Interfacial parameters can also be studied using the single fiber fragmentation test. This test consists of a single filament axially aligned in a epoxy tensile coupon which is loaded in tension. The tensile force on the coupon is transferred to the fiber through shear transfer at the interface. With increased loading, tensile forces exerted on the fiber exceed its tensile strength and the encapsulated fiber fractures into successively shorter lengths, eventually reducing the fragments to a critical shear transfer length, l_c. The distribution of fragment lengths has been determined to be satisfactorily described by a two-parameter Weibull analysis causing the expression for τ, the interfacial shear strength, to become:

$$\tau = \frac{\sigma_f}{2\beta}\Gamma(1 - 1/\alpha) \qquad (2)$$

where α and β are the shape and scale parameters, respectively, and Γ is the Gamma function. A more thorough account of the experimental analysis and technique can be found elsewhere.[12,13]

IV Determination of glass transition temperatures

Two methods were used to determine the glass transition temperature of samples used in this study. For bulk samples, a Differential Scanning Calorimeter (DSC, DuPont 9900) was used. DSC scans of cured matrices, as well as cured droplets, were made at 5°C/min under nitrogen purge using open pans. The glass transition temperatures were estimated from the midpoints of the transition regions. For individual as well as clusters of droplets too small to test on the DSC, a Thermal Mechanical Analyzer (TMA, DuPont, 9900) was used. This technique is a novel application of TMA, not attempted or found successful by others, for measuring thermal properties of very small quantities of polymer. Individual droplets were prepared on fibers as mentioned above and subsequently, after measurement of droplet dimensions, cut from the fibers and placed under the TMA probe for T_g determination. For droplets less than about 600 microns diameter, a cluster of droplets of similar size was used to generate the necessary signal for determining the T_g. The glass transition temperatures were estimated from the midpoints of the transitions. A careful check was made between these two experimental techniques to assure that consistent T_g's were obtained for identical samples.

DISCUSSION OF RESULTS

Initially an attempt was made to perform the microbond test after curing the m-PDA/DGEBA droplets with the "normal" curing cycle. For the AS4 fiber/m-PDA/DGEBA system the critical length in the fragmentation test is found[12] to be about 300 microns, so that the droplet sizes cannot be greater than about 200 microns for the microbond test to be successful. However, the experiments could not be completed because the smaller droplets (<110 microns) were incompletely cured as evidenced by the fact that they were "tacky" to the touch or "distorted" during initial stages of testing. To investigate this phenomenon more closely, the T_g of m-PDA/DGEBA droplets cured with the "normal" curing cycle was measured using the TMA as described above. The results are plotted in Figure 3 (triangular points) as droplet size *versus* T_g of the droplets. It can be seen that there is a strong correlation between droplet size and T_g. At small droplet sizes, the curing agent diffuses out of the samples, and the difference between the bulk T_g (T_g for the fully cured bulk DGEBA/m-PDA matrix is about 135–140°C) and T_g of the droplet is about 70°C. As the droplet size increases, the T_g of the droplet also increases until at a very large droplet size of about 600 microns the difference between bulk T_g and the droplet T_g is about 30°C. A recently published study by Rao and Drzal[14] has demonstrated that matrix modulus itself directly affects the interfacial shear strength. Since T_g reflects the matrix structure and hence its mechanical properties, the droplet mechanical properties change with size. Therefore, measurement of fiber-matrix adhesion by the microbond test can produce artifacts at small droplet size in systems with volatile components because of changes in droplet stoichiometry. For these systems, matrix properties have been shown to be dependent on droplet

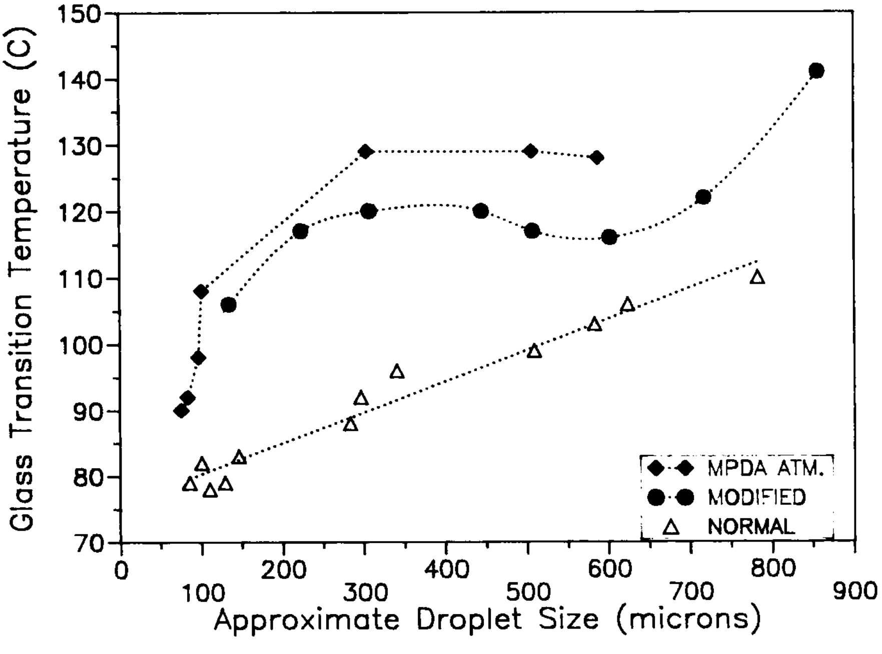

FIGURE 3 Glass transition temperature *versus* droplet size for various curing cycles and atmospheric conditions.

size. Thus, microbond tests will produce artifacts and cannot be run to get representative values of interfacial shear strengths for these systems unless account is taken of the change in material properties.

Since microbond tests failed when run with droplets cured with the "normal" cure cycle, an attempt to retard the process of diffusion and loss of the curing agent at high temperatures of cure was made. Droplets were cured with different, modified curing cycles as well as in m-PDA-rich curving environments. The experimental procedure, in the case of the systems in which a m-PDA atmosphere was used, was altered slightly. Droplet specimens were prepared as usual and mounted on frames; these frames were, in turn, placed inside a sealed glass chamber containing an excess of m-PDA at the bottom of the chamber. At processing temperatures the m-PDA melted and its vapor saturated the chamber. The droplets were then cured either with the normal or the modified curing cycles in contact with the m-PDA vapor. The various curing schemes are shown in Table I.

The variation of T_g with droplet size, for the different curing schemes, is shown in Figure 3. It can be seen that, at small droplet sizes (<150 microns), regardless of whether a m-PDA atmosphere or a modified curing cycle is used, the T_g is lower than the bulk T_g (even though it has increased when compared with the data from the "normal" curing cycle alone). At larger droplet sizes, the T_g has increased. However, the values are still low when compared with bulk values of T_g for this particular system. To estimate how much of the amine curing agent is

TABLE I
Experimental curing schedules and conditions for a DGEBA resin system cured with *m*-PDA curing agent

Curing scheme	Curing conditions	Amount of melted m-PDA in chamber	Microbond ISS (MPa)
A	75°C-2 hr 125°C-2 hr	6.667 g	38.9
B	75°C-2 hr 125°C-2 hr	37.423 g	36.8
C*	75°C-2 hr 125°C-2 hr	6.787 g	35.7
D	25°C-24 hr 75°C-2 hr 125°C-2 hr	6.699 g	45.3
E	25°C-24 hr 75°C-2 hr 125°C-2 hr	None	41.6
F	25°C-36 hr 75°C-2 hr 125°C-2 hr	None	54.7

Interfacial shear strength for these systems determined from the fragmentation test is 65–70 MPa.

* This mix contains twice the stoichiometric amount of m-PDA. All other mixes contain a stoichiometric amount of m-PDA.

TABLE II
Comparison of microbond and fragmentation test interfacial shear strengths for J-700/DGEBA system

Curing scheme	Microbond ISS (MPa)	Fragmentation ISS (MPa)
80°C-2 hr 125°C-3 hr	32.1	33.2

diffusing out of the droplets, a relationship between T_g and amount of curing agent (m-PDA) in the sample is necessary. The plot shown in Figure 4 used differential scanning calorimetry (DSC) to determine the relationship between amount of m-PDA in the bulk sample and T_g of the sample. By combining the data from Figures 3 and 4 an estimate can be made of the droplet m-PDA content as a function of droplet size. These data are plotted in Figure 5 where it is evident that, for the "normal" curing cycle, close to 40% of the amine curing agent has been lost in the small droplets. Even with the "modified" curing cycle, at small droplet sizes, about 25% of the amine curing agent is estimated to have been lost by diffusion. Ozzello *et al.*[15] and Haaksma *et al.*[16] have also made references to diffusion being a problem when conducting microbond tests though no attempts were made to quantify the phenomenon.

Because the modified curing cycle as well as the m-PDA-rich curing environ-

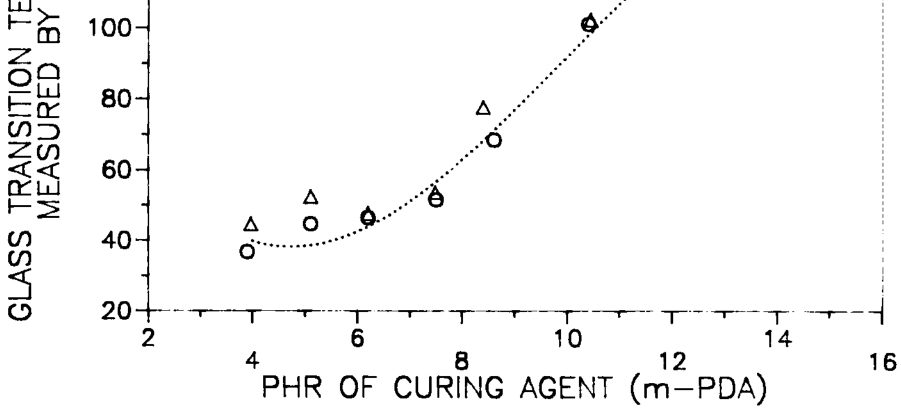

FIGURE 4 Glass transition temperature (as measured by DSC) *versus* the amount of curing agent used to cure the samples.

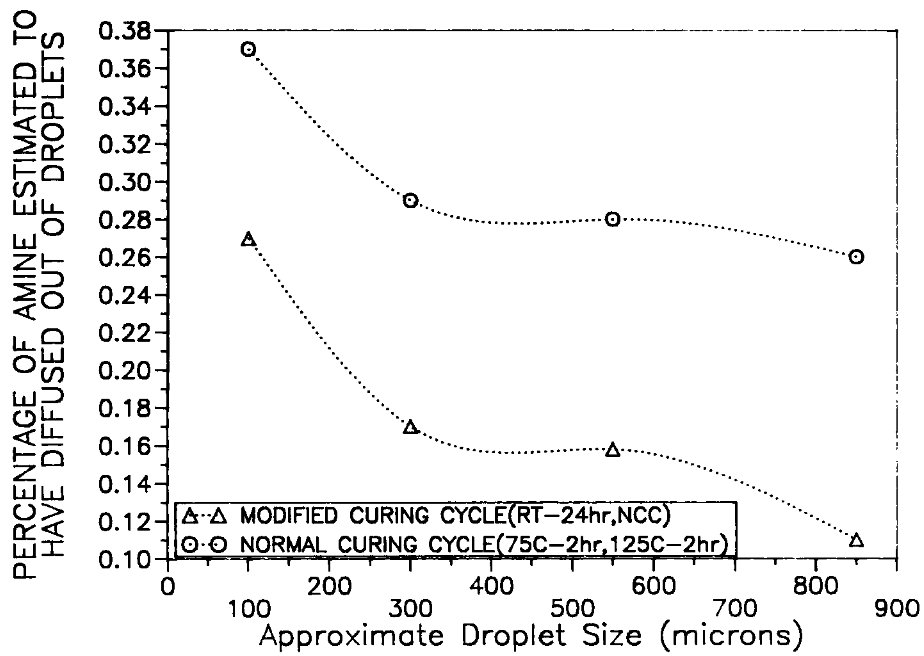

FIGURE 5 Fraction of amine curing agent estimated to have diffused out of droplets as a function of their size.

ment data showed less dependency of T_g on droplet size when compared with the normal curing cycle data, microbond experiments were conducted with various combinations of these conditions (Table I) to compare the fragmentation test with the microbond test. Systems cured with m-PDA and Jeffamine-700 diamine curing agents were chosen as the representative systems because previous[13] studies have been completed on these systems for determining the interfacial shear strength using the fragmentation test. Figures 6 and 7 all show the relationship between embedment area and debonding force, according to Equation (1), for the various curing schemes. In Figures 6 and 7, data are shown only for a limited range of embedment lengths. This is due to the fact that the carbon fibers tend to rupture if droplet sizes are greater than about one-half of the critical length determined from the fragmentation test. The range of data shown in Figures 6 and 7 corresponds to embedment lengths generally between one-third and one-half of the critical length. It can be seen that all the plots are linear in the range of testing and the values of interfacial shear strength (τ) shown in Table I represent the slope of the best fit line forced through the origin.

Figure 6 represents microbond data taken using curing schemes A through F listed in Table I and plotted in Figure 8. From Figure 8 it is evident that the microbond ISS (interfacial shear strength) calculated for all cases is low when compared with the corresponding fragmentation test result of about 65–70 MPa (fragmentation tests conducted on specimens subjected to curing schemes A–F all

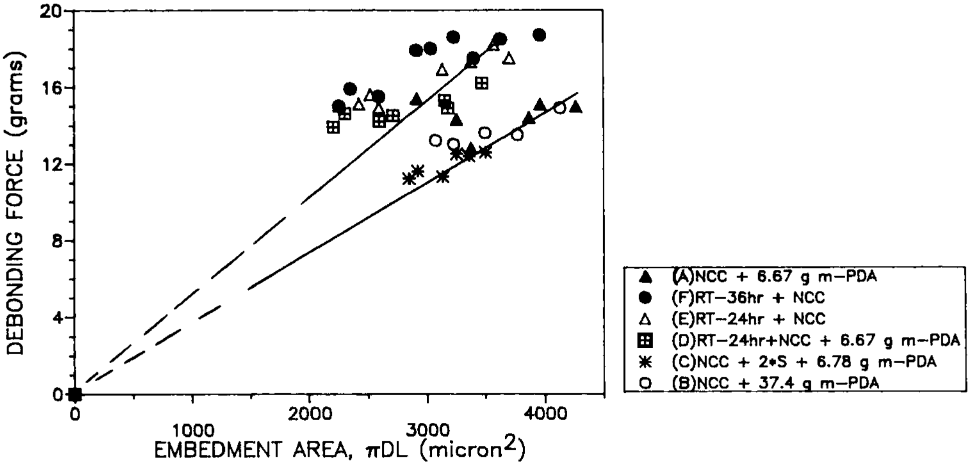

FIGURE 6 Force of debonding *versus* embedment area for the DGEBA/m-PDA/AS4 matrix/fiber system cured with different schedules and different atmospheric conditions.

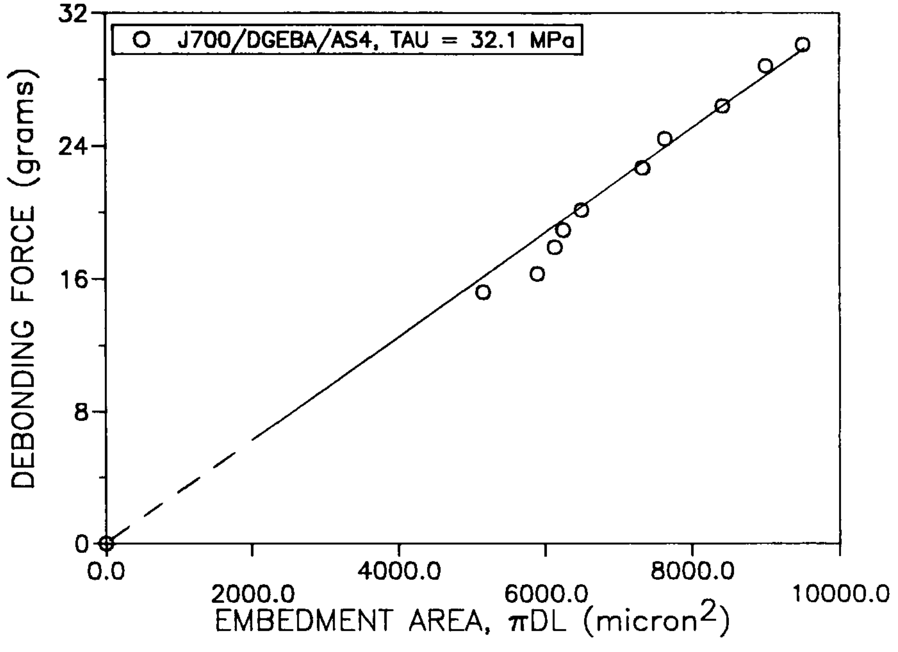

FIGURE 7 Force of debonding *versus* embedment area for the DGEBA system cured with a stoichiometric amount of Jeffamine-700 curing agent.

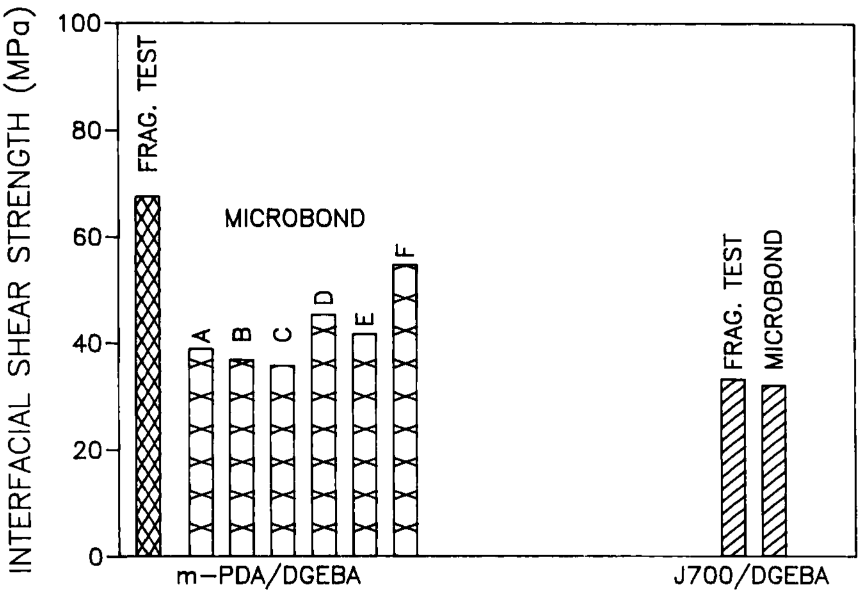

FIGURE 8 A comparison of the microbond and the fragmentation test for determining the ISS of the DGEBA/m-PDA system and the DGEBA/J-700 system.

showed a ISS between 65 and 70 MPa). The two lines shown in Figure 6 are representative of the data with (curing schemes A, B, and C) and without (curing schemes D, E and F) a room temperature cure portion. The lines illustrate the fact that with the room temperature cure the microbond ISS (the slope) has increased (for the microbond ISS values shown in Table I and Figure 8, however, individual "best-fit" lines through the origin for each set of data were used to calculated the slope and the microbond ISS).

The m-PDA environment (curing schemes A, B and C) is not able to retard the loss of m-PDA due to diffusion to any great extent. Changing the initial stoichiometry of the droplet (curing scheme C) also does not compensate for the amount of curing agent loss by the diffusion process. In curing schemes D–F, the "normal" curing cycle is preceeded by a room temperature cure portion. It can be seen from Figures 6 and 8 that the ISS's calculated for these curing schemes are slightly higher and thus closer to the ISS values measured using the fragmentation test. The room temperature step allows some reaction to occur between amine and epoxy which retards the diffusion process as indicated by the higher ISS results. Providing a m-PDA atmosphere does not seem to influence the results as evidenced by the fact that the data from Scheme D (with melted m-PDA environment) results in a lower ISS when compared with Scheme E (with no melted m-PDA). Scheme F, which has a 36 hour room temperature cure—compared with 24 hours in Schemes D and E—results in the highest microbond ISS measured. This again points to the fact that allowing the droplets to cure at room temperature before being exposed to a high temperature environment effectively causes the system to gel so that the loss of curing agent at high temperatures is reduced.

Figure 7 shows microbond data taken from another diamine curing agent system. In this case, a high molecular weight polyether diamine curing agent with reduced volatility was used and hence retarded the diffusion process. The data are shown in Figure 7 as embedment area *versus* force of debonding. The slope of the best fit line through the origin results in a microbond ISS of 32 MPa. From Figure 8 it can be seen that this value is within 5% of the ISS measured using the fragmentation test for this system.[14] These results are consistent with the fact that the J-700 curing agent has a lower vapor pressure and thus the amount of curing agent lost by diffusion and vaporization is minimized when compared with a more volatile system such as m-PDA/DGEBA. Figure 7 also shows that the range of embedment lengths tested with the J-700 system is greater than with the m-PDA systems. This is due to the J-700/DGEBA matrix being more compliant (the J-700 matrix has a strain to failure of about 98% while the m-PDA matrices have strain to failures of about 6%) leading to lower fiber-matrix adhesion. This lower adhesion allows larger drops to be tested (because the fiber does not tend to break) while the viscous nature of the J-700 curing agent allows for smaller drops to be tested. The scatter in Figure 7 is also seen to be much lower when compared with the scatter for the m-PDA systems tested.

Recent work done, using photoelastic and finite element analysis, by Herrera-Franco *et al.*,[17] has shown that the method of loading the microdrop in the droplet test affects the measured debonding force. The relative position of the blades with respect to the center of the drop (the contact angle between the blade and the microdrop) changes the stress distribution on the microdroplet. Thus, gripping the microdrop "incorrectly" may affect the measured debonding force. This is especially true for the brittle m-PDA systems studied; the J-700 curing agent gives a much more compliant matrix making blade location less critical. Thus, loading conditions may also contribute to the disparity between measurement of the interfacial shear strength by the two test methods.

CONCLUSIONS

Experiments were conducted to compare the embedded single fiber fragmentation test with the microbond test for determining the interfacial shear strength of carbon fibers in two different epoxy-amine thermoset matrices. Lack of agreement in the ISS between the fragmentation test and the microbond test has been attributed to loss of the curing agent by diffusion from small droplets ($<$ 150 microns) of resin which significantly changes the droplet mechanical properties. There is a strong correlation between droplet size and the amount of curing agent (m-PDA) lost. Droplets less than about 150 microns in diameter lose up to 40% of the curing agent by diffusion and evaporation during the "normal" curing cycle in which the droplets are exposed immediately to a high temperature. This loss of curing agent lowers the T_g of the droplets by 60°C. Adding excess curing agent to the curing atmosphere does not seem to reduce the loss of curing agent from the small drops. Modifying the cure cycle to include a protracted room temperature protion reduces the loss of curing agent. Microbond ISS values compare more favorably with fragmentation test ISS values after this modification. Less volatile curing agents (e.g. J-700) with the same resin and fiber result in close agreement between the two tests without modification of the cure cycle or the cure atmosphere. These results indicate caution must be exercised in use of the microbond test with certain polymer systems.

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NOMENCLATURE USED

τ	Interfacial shear strength (MPa)
F	Debonding force in the microbond test (MPa)
d	Measured diameter of fiber (μm)
L	Embedment length in microbond test (μm)
σ_f	Tensile strength of fiber (MPa)
α	Shape parameter in Weibull distribution
β	Scale parameter in Weibull distribution
Γ	Gamma function
πdL	Embedment area in microbond test (μm^2)