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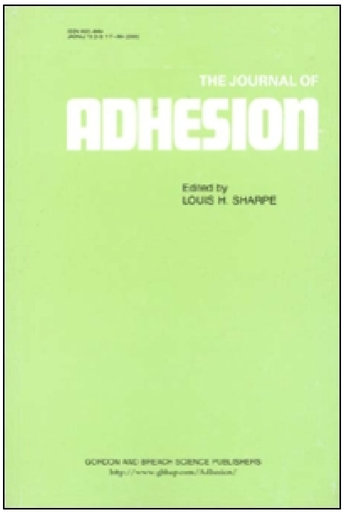

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Regeneration of Adhesive Bonding in Fiber/Resin Systems†

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The bond between a fiber and a surrounding polymer matrix can be weakened or completely broken by mechanical shearing. In some cases bond strength can be reduced by exposure to active environments (for example, hot water or steam). Obviously, it would be of considerable practical value if weakened or lost bonding could be regenerated. This paper presents the first results of an ongoing study of the possibility of bond repair in fiber/resin systems.

The use of the TRI microbond shear strength measurement technique makes it possible to study bond regeneration with individual fiber/resin specimens. Since the microdrop is displaced only a very short distance along the fiber during the shear strength measurement, it is a simple matter to treat a sheared drop without removing it from the fiber and then perform a second shear strength evaluation. Several systems have been studied in this manner, involving both thermosetting and thermoplastic resins. Examples of significant regeneration of both mechanically-sheared and hydrolytically-weakened bonds are given, and possible mechanisms for the bond strength regeneration are discussed.

KEY WORDS Fiber/polymer adhesion; microbond technique; bond regeneration; reversal of hydrolytic debonding; epoxy/fiber composites; thermoplastic/fiber composites.

INTRODUCTION

In many cases, the bond formed between a fiber and an encapsulating resin can be weakened by combinations of time, temperature, and exposure to certain environments. There is also the possibility that bond strength will be reduced by fatiguing processes, that is, the constant or cyclic application of stresses that are not large enough to produce instantaneous bond rupture. Finally, bonds can be completely destroyed by mechanical action that causes shearing or peeling. In each case, it should be of considerable technical value to determine if it were possible to regenerate all or part of lost bond strength by means of some aftertreatment.

Outwater and Gerry[1] have reported that split or cracked epoxy resin by itself can be "healed" by thermal treatment. Klosterman and Wool[2] showed that

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fatigued composites of polypropylene and polystyrene resins reinforced with short fibers also recovered strength on heating. Although these studies have shown that heating can cause macroscopic specimens to recover mechanical strength lost in fatiguing, we have not found published work that provides direct evidence for recovery of fiber/resin interfacial bond strength.

This paper deals with three types of potential fiber/resin bond regeneration: (1) recovery of strength loss resulting from hydrothermal processes, (2) rebonding of a cured thermoset to a fiber after the original bond has been sheared, and (3) regeneration of a sheared bond between a fiber and a thermoplastic resin by a second melting-solidification cycle.

EXPERIMENTAL DETAILS AND RESULTS

The TRI microbond method[3,4]

Our microbond technique involves the deposition of a small amount of resin onto the surface of a fiber in the form of a droplet which forms concentrically around the fiber in the shape of an ellipsoid. After appropriate hardening or curing, the fiber diameter and the droplet dimensions are measured with the aid of an optical microscope, and these measurements are used to determine the embedment areas. The fiber is pulled out of the resin using a special device to grip the droplet where it is bonded to the fiber (Figure 1). This device consists of two adjustable plates that form a slit, or microvise, which is attached to a vertical drive system. The plates are positioned just above the droplet, and the slit is narrowed symmetrically until the plates just make contact with the fiber. As the plates move downward, an initial frictional force between the fiber and the shearing plates is registered, indicating that the slit is just touching the fiber so that the droplet has little chance of slipping through. As the shearing plates continue to move downward, they encounter the droplet and exert a downward

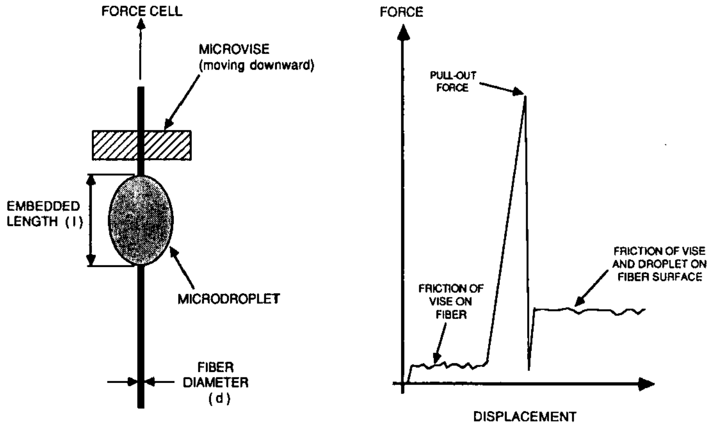

FIGURE 1 The microbond shearing arrangement and a typical force-displacement record.

shearing force on it. Upon debonding, the pull-out force is recorded, and the interfacial shear strength τ is calculated using the equation

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

where F is the measured debonding force, d the fiber diameter, and l the embedded length. Additional details of the microbond technique can be found in Refs 3 and 4.

Most procedures for determining bond strengths between fibers and resins are too destructive to permit any subsequent attempts at bond regeneration with the same specimen. However, the microbond shear strength determination results in only a very small displacement of the resin from its original contact location on a fiber. The resin remains around the fiber and, therefore, it becomes possible to try to form new bonds in fiber/resin specimens that have been debonded. After that, a second shear strength evaluation can be made. Microbond assemblies, moreover, can be more uniformly exposed to bond-weakening or bond-repairing environments than bulk composites.

Hydrothermal exposure of fiber/epoxy systems

Three fiber types were used for this part of the investigation: E-glass, Kevlar® 49, and a surface-modified Kevlar 49 (m-Kevlar 49) described elsewhere.[5] Droplets of an epoxy resin (Epon 828, Shell), which contained the curing agent 4,4-methylene dianiline (4:1 weight ratio), were deposited on these fibers and cured 2 hours at 80°C and then 2 hours at 150°C. Previous experiments have shown that when such systems are exposed to water at 88°C, all bond strength loss occurs within about one hour (Figure 2).[6] For the present studies, sets of

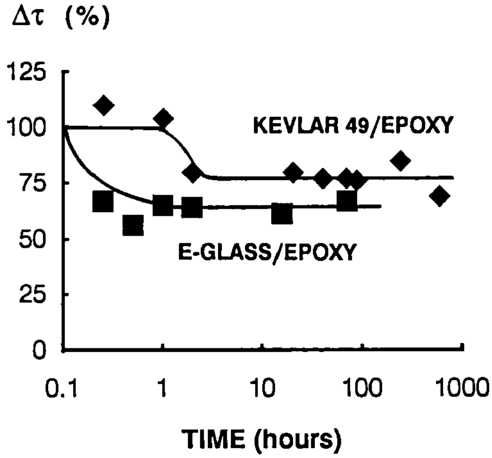

FIGURE 2 Relative change in bond strength after exposing Kevlar 49/epoxy and E-glass/epoxy microbnds to water at 88°C for successively longer times.

TABLE I
Regeneration of lost bond strength (MPa) on drying (Exposure or drying time 24 hours)

Treatment	E-glass/ Epon 828	Kevlar 49/ Epon 828	m-Kevlar 49/ Epon 828
Untreated control	43.5	41.4	57.1
Exposure to H_2O @ 88°C,	27.4 (63%)	31.8 (77%)	49.4 (87%)
and drying at 115°C	35.2 (81%)	43.8 (106%)	58.2 (102%)
Drying at 115°C only	41.2 (97%)	36.8 (89%)	—

TABLE II
Effect of hydrothermal exposure and drying on the shear strength (MPa) of silanized E-glass/epoxy bonds (Initial shear strength = 64.8 MPa)

	Hydrothermal exposure time		
	2 hours	16 hours	40 hours
Exposure to H_2O at 88°C	63.6 (98%)	55.3 (85%)	45.0 (69%)
Subsequent drying at 115°C for 24 hours	55.0 (85%)	50.1 (77%)	41.3 (64%)
Drying at 115°C only	—	—	46.0 (71%)

cured fiber/resin microdroplet specimens were exposed to these conditions for 24 hours, and their bond strengths evaluated. Control sets of specimens were maintained for the same period and also tested.

The results of the hydrothermal exposure can be seen by comparing the first and second lines in Table I. These data were obtained with half of each collection of exposed specimens (that is, at least 30 individual specimens were measured). The remaining specimens were dried by storing them in a vacuum oven at 115°C for 24 hours. The consequences of this drying treatment are shown in the third line of the table. In each case, lost bond strength was recovered, only partially by the E-glass fibers, but completely by the Kevlar. Drying unexposed specimens for 24 hours at 115°C by itself causes no increase in bond strength, as can be seen from the data in the last line of Table I.

A similar study was made of the effects of hydrothermal aging and drying on a silane-treated E-glass fiber combined with the same epoxy matrix. The silane treatment consisted of exposure to a 0.01 M solution of γ-glycidoxypropyltrimethoxysilane (A-187, Union Carbide). The results (Table II) show that, in this case, loss of bond strength with hydrothermal exposure was more gradual than with untreated E-glass, and there was no recovery of strength on drying; in fact, the dried bonds were even weaker than their undried predecessors. Furthermore, the strength loss after vacuum drying by itself was about the same as that due to hydrothermal exposure. Here it appears that bond deterioration follows from thermal energy input without much influence from the water.

Rebonding of sheared fiber/epoxy pairs

A master batch of sixty Epon 828 droplets deposited on Kevlar 49 filaments was prepared. As before, the droplets were cured at 80°C for 2 hours followed by 150°C for 2 hours. Bond strength was measured for each specimen using the microbond method, each sheared droplet remaining around the fiber. Then the collection of sheared filament/droplet assemblies was separated arbitrarily into two batches of thirty assemblies each, which were stored at room temperature. After 30 days, one batch was tested with the microbond shearing vise. No significant pull-out force could be observed for any of these specimens. The other group was submitted to the same thermal treatment as before, i.e., they were "recured." These recured specimens showed conventional pull-outs and appreciable pull-out forces. The results of recuring are shown in Figure 3 and in Table III.

A similar study was performed with the surface-modified Kevlar fibers, which exhibited stronger initial bonding with the epoxy (57.1 MPa). Shearing and recuring this combination produced an average bond strength of 23.7 MPa, which was essentially the same as what could be regenerated with the conventional Kevlar 49.

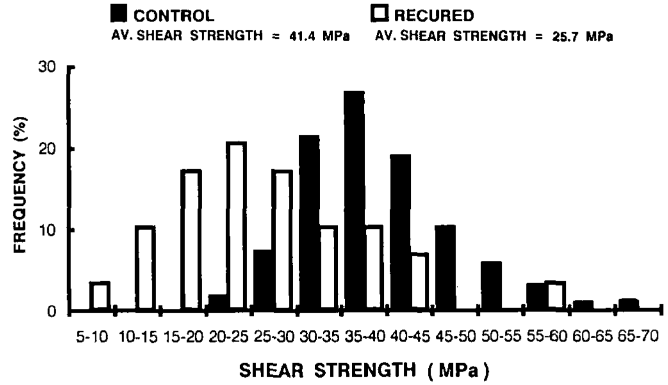

FIGURE 3 Effect on shear strength distribution of recuring sheared Kevlar 49/epoxy microdroplet assemblies.

TABLE III
Results of recuring sheared Kevlar/epoxy bonds

	No. of specimens	Avg. shear strength, MPa ±95% conf.
Initial collection	59	41.4 ± 2.9
Recured after 30 days	29	25.7 ± 3.3 (62%)
Stored 30 days at room temp.	30	not significant

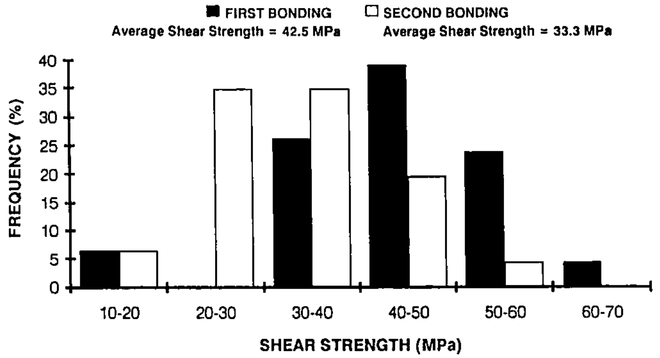

FIGURE 4 Distributions of bond strengths for first and second bondings of 46 Kevlar 49/polycarbonate microassemblies.

Reforming of sheared fiber/thermoplastic bonds

Polycarbonate resin droplets were formed by melting the polymer film (Rodyne T302 from Coburn Corp.) onto Kevlar 49 filaments. The droplets were kept at 275°C for 2 hours and solidified by cooling at the rate of approximately 1°C/min.[7] Forty-six fiber/droplet specimens were prepared, and their bond strengths measured. As a result of the measurement, each droplet was moved to a new site on the fiber no more than 2–3 mm away from its original location. They were then remelted and resolidified using the same time/temperature program and the new bond strengths determined. The results for the first and second bondings are compared in Figure 4. The average bond strength for the second bonding was somewhat lower than that for the first (33.3 as compared to 42.5 MPa), and the distributions of bond strengths also were not the same.

DISCUSSION OF RESULTS

Hydrothermal processes

Both physical and chemical processes have been proposed to explain the bond weakening effect of water on fiber/epoxy bonds.[6] Absorption of water may swell the epoxy, causing it to move away from the fiber. Or else, the cohesive strength of the resin may decrease so that friction due to mechanical interlocking is reduced. Following from either of these, if the water is removed by vacuum drying, it is not surprising that the bond strength would return to its original value, as was the case with the two Kevlar fibers. From the data shown in Table I it is seen that the absolute reduction in bond strength for the two Kevlar fiber systems is the same (~8 MPa), even though the surface-treated fiber bonded much more strongly to the resin. This suggests that the water affected only bulk properties of the resin in these two cases.

With glass fiber, however, the hydrothermal effect produced a larger drop in bond strength that was not completely reversible, which suggests that a chemical process has occurred also and that it cannot be nullified by subsequent drying. The silane treated glass fibers formed a bond that had quite a different response. The drop in bond strength was about the same for both dry and wet heating and no recovery was effected by removal of absorbed water.

Sheared epoxy bonds

There are three possible explanations for the appreciable bond strength that can be regenerated after a cured epoxy droplet is debonded and moved to a new location: (1) Residual epoxy functionality is still available and is activated by the second thermal treatment, producing new chemical bonding with the fresh fiber surface. (2) The rupture of primary chemical bonds caused by the shearing process results in more and possibly different chemically reactive sites on the contacting surface of the epoxy drop. These sites may instigate new chemical links across the interface when the drop/fiber combinations are reheated. (3) Mechanical bonding caused by differential thermal shrinkage or by the flow of heat-softened epoxy into surface crevices could produce significant shear debonding resistance.

The first of these explanations has been investigated by carrying out a recuring study in which Kevlar/epoxy bonds were put through four shearing/recuring cycles. The results are shown in Figure 5. Each time the recovered bond strength was about the same, which clearly suggests that residual epoxy functionality cannot be a factor, since it is very unlikely that there would be any left after the first recuring. The complementary experiment with the surface-modified Kevlar that produced a higher bond strength originally but gave the same amount of bonding on recuring suggests that mechanical bonding is the primary cause of the rebonding.

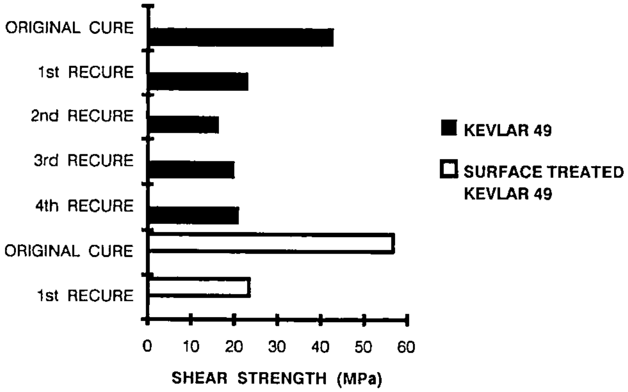

FIGURE 5 Shear strength of Kevlar 49/epoxy microdroplet assemblies after multiple shearing–curing cycles.

Reforming fiber/thermoplastic bonds

It is not surprising that sheared thermoplastic droplets can form bonds when remelted, because with such materials the bonding is understood to be due to some combination of mechanical friction and secondary chemical attraction (e.g., acid-base interactions). Both types of bonding would be reactivated by a second melt–solidification cycle. The average bond strengths and distributions shown in Figure 4 suggest that the second bonding may not be the same as the first, but it is not possible to form any general conclusions without additional data. It should be kept in mind that the fiber surface may have been altered by the heating used to produce the first bond, so that the second time we would be dealing with a different condition.

SUMMARY AND CONCLUSIONS

It has been demonstrated that lost bonding can be regenerated, or new bonding produced, by simple thermal treatments of fiber/resin microbond assemblies. The effect of water on fiber/epoxy bonds depends on the nature of the fiber. Glass/epoxy bonds are weakened more than Kevlar/epoxy bonds and, in contrast to the latter, are not completely recoverable on drying. A silane-treated glass did not show any bond regeneration on drying. Sheared fiber/epoxy bonds recover an appreciable fraction of their original shear strength on heating; more experimental studies are needed to establish whether this is due to mechanical processes or if there is any new chemical bonding in these cases. As expected, remelting sheared fiber/thermoplastic bonds produces rebonding. However, it seems that this second bonding is not the same as the first, possibly because the fiber has a different thermal history the second time around.

Acknowledgments

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References

1. J. O. Outwater and D. J. Gerry, *J. Adhesion* **1,** 290 (1969).
2. D. H. Klosterman and R. P. Wool, *Am. Phys. Soc. (High Polymer Physics) Abstracts* **27,** 361 (1982).
3. B. Miller, P. Muri and L. Rebenfeld, *Comp. Sci. Tech.* **28,** 17 (1987).
4. U. Gaur and B. Miller, *Comp. Sci. Tech.* **34,** 35 (1989).
5. G. C. Tesoro, R. Benrashid, L. Rebenfeld and U. Gaur, in *Proc. IUPAC Conf. on Polymers for Advanced Technologies,* Jerusalem, Israel, 1987.
6. U. Gaur and B. Miller, *Polymer Composites,* submitted for publication.
7. U. Gaur, G. P. Desio and B. Miller, *Proceedings of 47th SPE Annual Technical Conf.*, p. 1513 (1989).