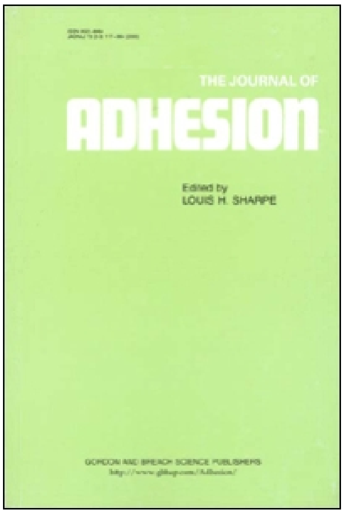

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Regeneration of Interfacial Adhesion in Fiber Reinforced Composites

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Our studies of the regeneration of interfacial adhesion in micro-composites have shown that fiber/thermoplastic (aramid/polycarbonate) bonds can be completely regenerated, the degree of regeneration depending on both time and temperature of heating. Complete regeneration requires high temperatures, suggesting that mechanical interlocking resulting from flow of heat-softened resin into fiber surface crevices may be the primary mechanism of bond strength regeneration. Only partial regeneration of fiber/thermosetting resin (epoxy with aramid and carbon fibers) bond strength has been achieved, and this appears to be independent of fiber and reheating time. Apparently, the viscoelastic behavior of the resin is a critical factor in bond strength regeneration.

Keywords: Interface; fiber; resin; bond regeneration; adhesion

INTRODUCTION

Composite materials can be considerably weakened or completely damaged due to fatigue, mechanical impact or exposure to hostile environments (*e.g.*, hot water). It would be of considerable practical value if all or part of such lost strength could be regenerated by some post-treatment. In general, the damage resulting from the hostile environments can be classified into two types: fiber damage and matrix damage. Fiber damage includes breakage of single filaments embedded in resin and laminate puncture, while matrix damage includes fiber/matrix separation, crack propagation in resin, delamination, etc.

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One would expect that it is easier to "repair" damage to a resin than to a fiber. The use of different heat generation techniques for fusion bonding of thermoplastic composites, including induction heating [1], focused IR heating and resistance heating [2, 3] ultrasonic welding [4] vibration welding [5] and thermobond interlayer bonding [6] has been reported. Outwater and Gerry [7] reported that split or cracked thermoset resin (epoxy) can also be "healed" by thermal treatment. All these studies showed that a thermal treatment can recover part or all of the mechanical properties of a composite by "repairing" the damage in the resin. However, the only direct evidence of bond regeneration at a fiber/matrix interface was reported by Miller and Gaur [8]. Their investigation showed that significant interfacial bond strength regeneration of both mechanically-sheared and hydrothermally-weakened bonds, involving both thermosetting and thermoplastic resins, is indeed possible. It was noted that sheared fiber/epoxy bonds recover an appreciable fraction ($\sim 60\%$) of their original strength after re-exposure to the same heating conditions used for the original curing. Also, re-melting the resin produced significant rebonding ($\sim 78\%$) with sheared fiber/thermoplastic bonds. In this study, we investigate the recovery of interfacial bonding for different systems under various bond regeneration conditions. The focus of these investigations is to further our understanding of the mechanism(s) of rebonding in such composites.

The TRI microbond technique for measuring interfacial shear strength (IFSS) makes it convenient to study bond regeneration with individual fiber/resin specimens. Since the microdroplet is displaced only a very short distance along the fiber during the shear strength measurement, it is a simple matter to reheat a sheared droplet without removing it from the fiber and then perform a second shear strength evaluation.

EXPERIMENTAL

Microbond specimens were prepared by depositing small droplets of resin on single filaments. After solidification of the resin droplet, a movable microvise is applied to the droplet to pull the fiber out from the resin. The force required to debond the interface is recorded and the IFSS is computed as the ratio of the debonding force to the contact area. Details of this microbond technique using thermoset and thermoplastic resins are reported in References 9 and 10, respectively. At first, Kevlar 49®/polycarbonate (PC) and Kevlar 49/epoxy systems were studied. The regular (control) processing conditions for the two systems are listed in Table I. Large batches of microbond specimens were prepared for all the systems under regular processing conditions to obtain the original IFSS values and to provide debonded specimens for bond regeneration.

After the microbond specimens were debonded, they were placed in an oven and reheated isothermally for different time intervals ranging from 5 minutes to 1 week to regenerate interfacial bonding.

These specimens were then tested again using the same technique at room temperature and the regenerated bond strengths evaluated. Additional bond regeneration studies with epoxy resin were performed with AS4, HMS carbon fibers (Hercules) and pitch fiber (Tonen HM pitch-based).

RESULTS AND DISCUSSION

Thermoplastic Resin

Results of bond regeneration experiments on Kevlar 49 embedded in PC are summarized in Table II. The data show that the regeneration of bond strength is dependent on both processing time and processing temperature, which is consistent with the work reported by Brady and Porter [11]. When the specimens are kept at 250°C or 275°C for at least 20 minutes, complete regeneration of the bond strength takes place. This supersedes our earlier observation that only partial bond regeneration is achievable in thermoplastic composites [8]. At lower

TABLE I Processing Conditions of Resins

Resin	*Processing conditions*
PC (polycarbonate from Coburn)	275°C for 30 min
Epoxy (Epon 828 from Shell) cured with methylene dianiline (wt. ration 4:1)	80°C for 2 hours followed by 150°C for 3 hours

TABLE II Regenerated IFSS (MPa) as a Function of Processing Conditions

	Kevlar 49/PC (Original IFSS = 34.8 MPa)				
Time↓/Temp→	*275°C*	*250°C*	*225°C*	*200°C*	*180°C*
5 minutes	31.8	28.5	~0	~0	~0
20 minutes	—	35.0	15.6	11.7	~0
30 minutes	36.5	38.2	16.7	19.9	15.6
1 hour	37.9	36.0	25.0	23.2	17.1
2 hours	33.0	38.1	29.9	23.5	—
3 hours	—	—	32.0	—	18.3
6 hours	—	—	—	26.2	10.8
1 day	—	—	27.0	28.5	15.9
3 days	—	—	32.5	34.8	20.4
1 week	—	—	—	—	24.0

Note: 1. At least 15 specimens were tested at each condition
2. Typical 95% confidence level ranges from 5% to 10% of the average value.

temperatures, longer times are required to regenerate significant bond strength, and the regenerated bond strength increases with processing time. The data also show that complete regeneration of bond strength can be accomplished only by processing the specimens above 200°C, below 200°C, bond strength cannot be completely regenerated even by heating for one week.

To understand the mechanism of bond strength regeneration through heating, we first consider microbond specimens at different temperatures before and after debonding. When a microbond specimen is cooled from its initial processing temperature, the resin hardens and, if the resin has a larger thermal expansion coefficient than the fiber, it will shrink more than the fiber does, inducing a radial compressive force at the interface. After the microbond specimen is debonded at room temperature, the compressive force still exists as evidenced by the presence of the considerable frictional force observed on the debonded specimen when the droplet is moved along the fiber by the microvise. In the bond regeneration process, as the debonded specimens are heated to an elevated temperature, the resin becomes soft. The compressive force at the interface will then deform the softened resin, forcing it to form better contact with fiber. However, at an elevated temperature, due to its larger thermal expansion coefficient, the resin expands more than the fiber, causing a reduction of the compressive force at the interface. Therefore, the level of bond strength recovery should be a competition between the softening of resin and the compressive force at the interface. In fact, once the temperature is higher than the stress-free temperature, the compressive force should be negative since the resin expands more than the fiber and starts to separate from the fiber surface.

The time-temperature superposition of experimental data shows that a higher regeneration temperature gives faster bond strength recovery rate, suggesting that the bond strength regeneration mechanism is dominated by the softening of the resin (*i.e.* the viscoelastic behavior of the resin), which produces better contact between the resin and fiber surface.

Since interfacial shear strengths for the original bond (processed at 275°C) and the bonds regenerated at the same temperature are the same, the data further imply that the initial heat treatment of the Kevlar 49 fiber surface does not affect its subsequent bonding to PC.

Thermosetting Resin

For a thermosetting resin such as the epoxy, only partial regeneration of bond strength could be achieved. Earlier experiments with Kevlar 49 fiber have shown that on reheating, using the original curing conditions (2 hours at 80°C and 3 hours at 150°C), only 54% of the bond strength is regenerated [8]. Four subsequent shearing/reheating cycles resulted in about the same level of bond strength recovery (see Fig. 1). Based on the facts that there is no residual epoxy functionality left on the surface of the fully-cured resin, and that the same levels of bond strength were recovered regardless of the number of processing cycles, we concluded that the rupture of chemical bonding at the originally-formed interface was not recoverable and that the partially recovered bond strength is from mechanical interlocking at the interface.

Further experiments with the Kevlar 49/epoxy system have been conducted using various combinations of reheating time and temperature. The regenerated bond strengths are summarized in Table III. The data show that for a Kevlar 49/epoxy system at a specific reheating temperature, a characteristic percentage of bond strength was regained within 1 hour. However, for more than 1 hour reheating time, bond regeneration was virtually independent of processing time. It is of interest to note that bond regeneration at temperatures below the glass transition temperature of Epon 828® (155°C) consistently results

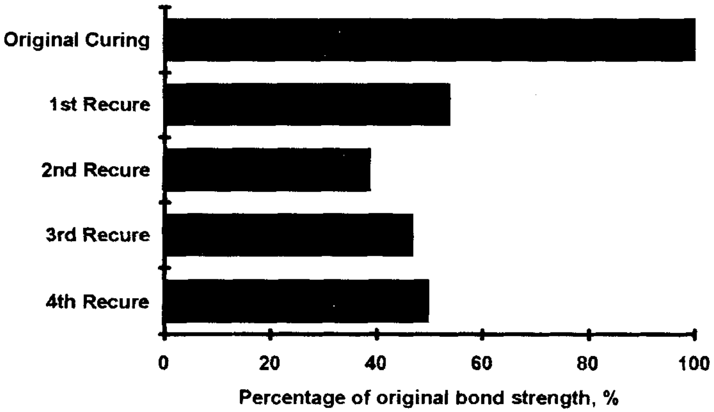

FIGURE 1 Shear strength of Kevlar 49/epoxy microdroplet assemblies after multiple shearing curing cycles [8].

TABLE III Regenerated IFSS (MPa) as a Function of Processing Conditions

	Kevlar 49/epoxy (Original IFSS = 32.7 MPa)						
Time↓/Temp→	*Room Temp.*	*80°C*	*120°C*	*150°C*	*165°C*	*180°C*	*195°C*
1 hour	~0	9.5	11.0	8.3	16.2	18.6	20.1
4 hours	~0	11.7	8.8	9.3	–	18.4	18.3
8 hours	~0	–	–	11.2	–	–	–
1 day	~0	12.6	10.8	11.7	–	17.4	–
4 days	~0	–	11.3	–	–	–	–

Note: 1. At least 15 specimens were tested at each condition,
2. Typical 95% confidence level ranges from 5% to 10% of the average value.

in about 30% bond strength regeneration while 60% of the original bond strength is regenerated by processing above 180°C. It is apparent that this temperature dependence is related to the softening of the resin. It is possible that at the beginning of reheating process at lower temperatures, the high compressive force at the interface forces the slightly softened resin to flow into some relatively rough crevices on the fiber surface to increase the level of mechanical interlocking at the interface. However, because of its low mobility, the resin needs a much longer time to flow into the fine crevices on the fiber surface to achieve a higher level of mechanical interlocking. The higher bond strength recovery at 180°C than at 150°C (60% *vs.* 30%) can be explained by the relatively higher mobility of the cured epoxy at 180°C.

Since the presence of the fiber may affect the curing of epoxy resin in the interfacial region [12], it is conceivable that the resin in the interfacial region exhibits a much lower T_g than the bulk resin. Therefore, another possible explanation of having a consistent 30% bond strength recovery at temperatures lower than the T_g of the resin is that the interfacial zone, with a lower T_g, becomes soft at a lower temperture. The softened resin regains better contact with the fiber, resulting in limited interfacial bond strength recovery. At processing temperatures higher than 180°C, the bulk resin softens, resulting in more bond strength recovery.

Carbon Fibers

Table IV shows the bond regeneration data for different fiber/epoxy systems. The percentage of bond strength recovery with epoxy resin rank as:

$$\text{pitch} > \text{Kevlar49} \approx \text{AS4} \approx \text{HMS}$$

Representative SEM micrographs of these fiber surfaces, as shown in Figure 2, seem to imply that the bond regeneration phenomenon for epoxy resin depends on the structure of the fiber surface. Based on their appearances, the fibers can be classified into two groups. The surfaces of Kevlar, AS4 and HMS are essentially featureless and smooth, while the surface of the pitch-based fiber is noticeably different, with striations or grooves along the fiber. As we have argued earlier, the regenerated bond strength is mainly due to the higher level of mechanical interlocking between the fiber and resin, resulting from

TABLE IV IFSS Values of Different Fiber/Epoxy Systems Bond Regeneration was Conducted at 180°C for 1 hour. MPa (Avg. ± 95% conf.)

Fiber	*Original IFSS*	*Regenerated IFSS (% of orig. IFSS)*
Kevlar 49	32.7 ± 1.3	18.6 ± 4.1 (57)
AS4	44.9 ± 3.3	25.2 ± 5.1 (56)
HMS	29.9 ± 3.1	17.0 ± 1.9 (57)
Pitch	15.6 ± 1.6	12.4 ± 2.0 (79)

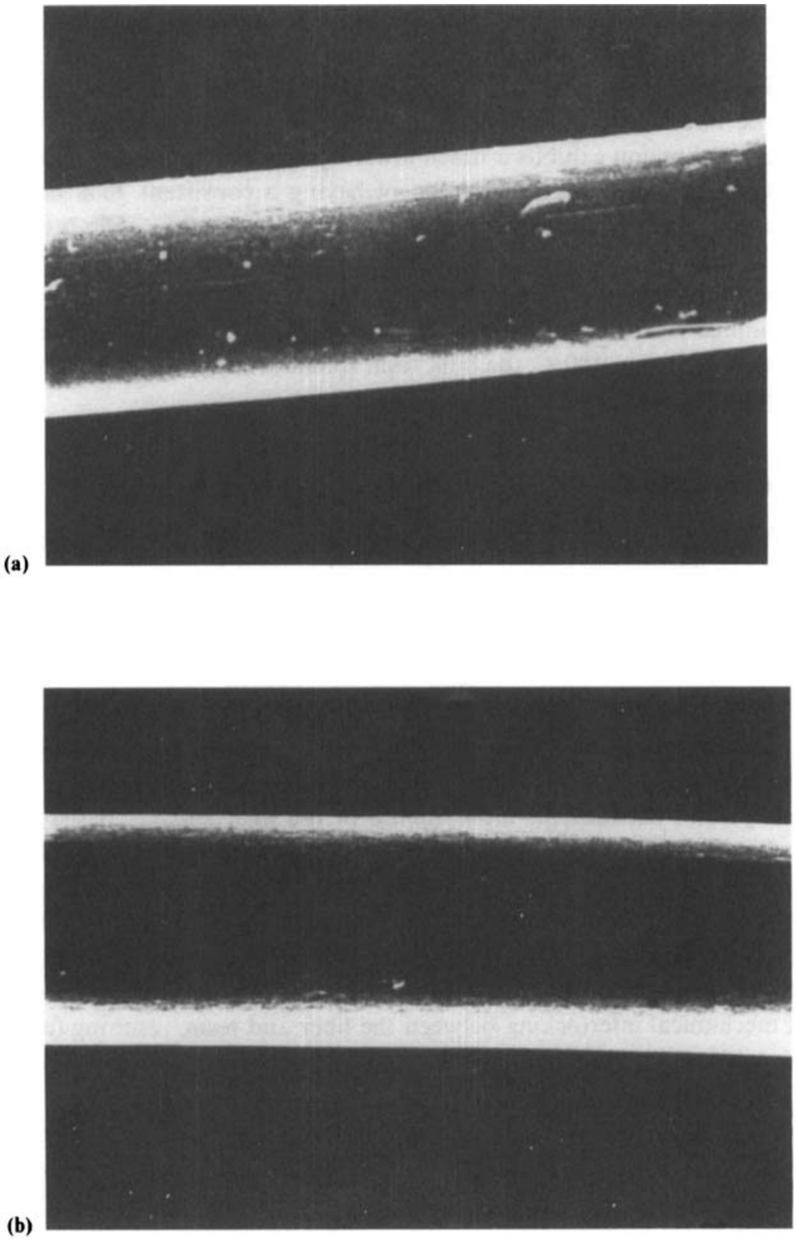

FIGURE 2 Representative SEM micrographs of Kevlar, HMS and Pitch fiber surfaces; a) Kevlar (2400x); b) MS carbon fiber (3600x); c) Pitch graphite fiber (2300x).

(c)

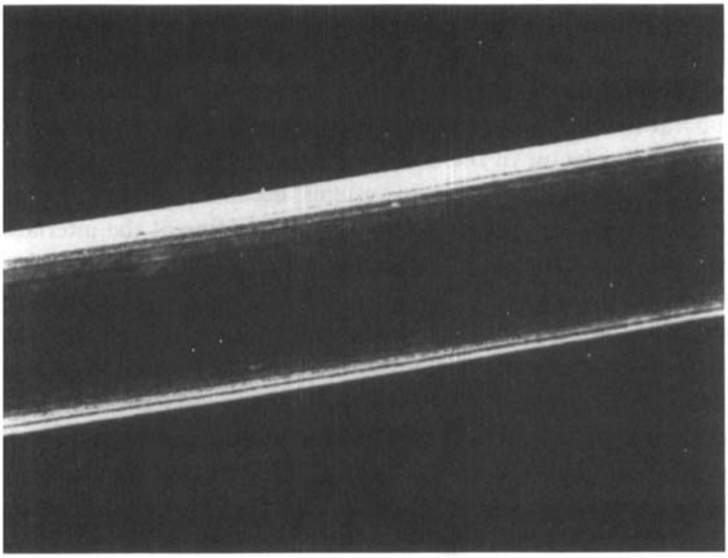

FIGURE 2 (Continued).

the flow of heat-softened resin into fiber surface crevices at elevated temperature. It is, therefore, expected that, under an identical bond regeneration condition, the level of regenerated bond strengths for the three fibers with similar smooth surfaces should be very similar, as evidenced by the experimental data. For the pitch-based fiber, the higher bond strength recovery for the straited fiber is possibly a consequence that at 180°C, the softened epoxy resin was able to flow into the grooves to achieve a higher level of mechanical interlocking.

Another important feature of the bond strength regeneration is that that bond strengh is regenerated uniformly along the interface, as we reported earlier [13].

CONCLUSION

We have demonstrated that a fractured fiber/matrix interface can be "repaired" through thermal treatment of the debonded microcomposites. The experimental data show that full recovery of interfacial bond strength can be achieved for a fiber/thermoplastic resin system.

The regenerated bond strength depends on both the processing temperature and processing time. A higher level of bond strength recovery can be obtained by processing the debonded specimens at a higher temperature and/or for longer time. The viscoelastic behavior of the resin is a key factor in the bond regeneration behavior.

For fiber/thermosetting resin systems, because of certain irreversible processes, possibly rupturing of chemical bonding at the interface, the bond strength can be only partially regenerated. We have also observed that the level of regenerated bond strength for a thermosetting resin seems to be dependent on the structure of the fiber surface.

It is concluded that mechanical interlocking at the interface is the primary mechanism of the regained adhesive strength between fiber and resin after the thermal treatment. Examining the failure mode of the "original" and "regenerated" interfaces, we conclude that the bond was regenerated uniformly along the interface with processing time.

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