Toughening of Epoxy Resin by Reacting with Functional Terminated-Polyurethanes

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SYNOPSIS

Hydroxyl-, amine-, and anhydride-terminated polyurethane (PU) prepolymer which were synthesized from polyether (PTMG) diol, 4,4′-diphenylmethane diisocyanate (MDI), and a coupling agent bisphenol-A, 4,4′-diaminodiphenyl sulfone (DDS), or benzophenonetetracarboxylic dianhydride (BTDA) were used to modify the toughness of bisphenol-A diglycidyl ether epoxy resin (DGEBA) cured with 4,4′-diaminodiphenyl sulfone. From the experimental results, it was shown that the modified resin displayed a significant improvement in fracture energy (G_{IC}) and also in its interfacial shear strength with polyaramid fiber. It was more enhanced with increase of the PU modifier wt % content. The hydroxyl-terminated PU was found to be the most effective among those three prepolymers. In addition, the toughening mechanism was discussed based on the morphological and the dynamic mechanical behavior of the modified epoxy resin. Fractography of the specimen observed by transmission (TEM) and scanning electron microscopy (SEM) revealed that the modified resin had a two-phase structure. The existence of an unclean fiber surface after its fiber pullout test suggested that a ductile fracture might have occurred. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy resins are often utilized as the matrix in a composite because of their high mechanical properties, high chemical resistance, and excellent dimensional stability. But their low toughness, especially in the presence of sharp cracks, detracted from their application. Several methods[1-3] had been proposed to increase the toughness of the epoxy network and one of the most successful routes was to incorporate a second phase of dispersed rubbery particles into the crosslinked network. The primary factor of the rubber-modified matrix is the necessity to have a chemical linking of the rubber with the resin: It is not only to increase the molar mass of the rubber, which leads to a phase separation, but also to ensure their intrinsically strong chemical bonds across the rubbery phase/resin matrix interface. Otherwise, a premature failure at the particle–matrix interface, due to the presence of high stress concentration at the boundary, will occur.

Moreover, Chiao and co-workers[4] indicated that the interlaminar shear and transverse tensile strength of a composite were highly dependent upon the toughness of matrix resins and also upon the properties of the fiber/matrix interface, which played an important role in controlling the mechanical properties of the composite. The surface treatments and coupling agents developed for glass and graphite reinforcements that increase interfacial strength by two to three times over untreated composites have been studied.[5,6] Those surface modifications also provide increased hydrothermal stability. Unfortunately, similar promoting bonding methods are not readily available for a polyaramid-reinforced composite system. Consequently, interface-sensitive properties are weaker in the polyamide-containing system than are those of their glass or graphite counterparts.[7,8] Thus, the low off-axis properties of polyaramid-reinforced composites give numerous investigations to improve the filament–matrix adhesion.[9,10]

In the present study, we attempted to toughen the epoxy network using polyurethane (PU) as the modifier, which could cause a substantial increase in interfacial shear strength (IFSS) of the polyar-

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amid fiber/epoxy matrix interface. The problem of chemically linking the modifier to the epoxy network was overcome by using bisphenol-A (Bis-A), 4,4′-diaminodiphenyl sulfone (DDS), or benzophenonetetracarboxylic dianhydride (BTDA) as a coupling agent between the PU and the epoxy oligomer.

EXPERIMENTAL

Materials

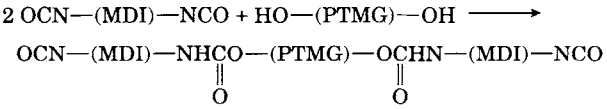
Polytetramethylene glycol (PTMG 2000) was kindly supplied by Evermore Chemical Industry Co. 4,4′-Diphenylmethane diisocyanate (MDI), bisphenol-A (Bis-A), benzophenonetetracarboxylic dianhydride (BTDA), and 4,4′-diaminodiphenyl sulfone (DDS) were purchased from Merck Co. All materials were used as received.

Dimethylacetamide (DMAc) was first distilled over CaH_2 at 90°C/10 mmHg and then stored in the molecular sieves. The bisphenol-A diglycidyl ether-type epoxy resin (Epon 826) was obtained from Shell Chemical Corp. (equivalent wt = 190 g/mol). The hardener diaminodiphenyl sulfone (HT976) was obtained from Ciba-Geigy Corp.

Synthesis of Functional Terminated-PU Prepolymer

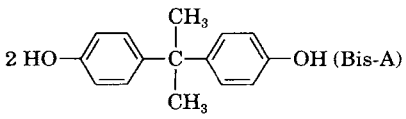
The functional terminated-PU prepolymers were prepared by reacting 2 equivalents of MDI with 1 equivalent of macroglycol (PTMG 2000) in DMAc. The reaction was carried out under nitrogen at 70–75°C and the isocyanate content (determined by the di-*n*-butylamine titration method) was reached. Subsequently, this oligomer was reacting with 2 equivalents of the coupling agent (Bis-A, DDS, or BTDA) at 80°C for 4 h. The reaction products were dried at 80°C for 48 h in a vacuum. This reaction scheme is shown as follows:

Step 1.



PU oligomer

Step 2.



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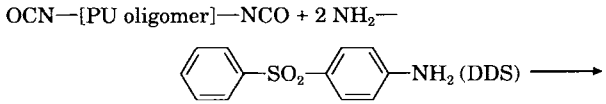

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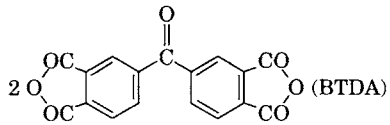

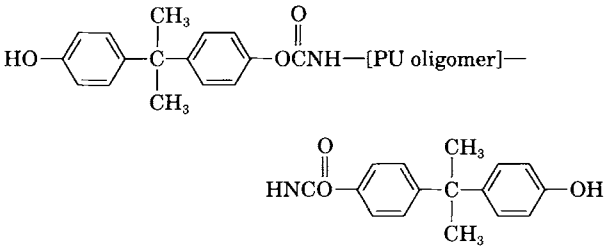

Hydroxylic-terminated prepolymer (HTPU)

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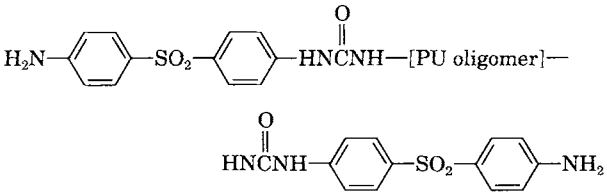

Amine-terminated prepolymer (ATPU)

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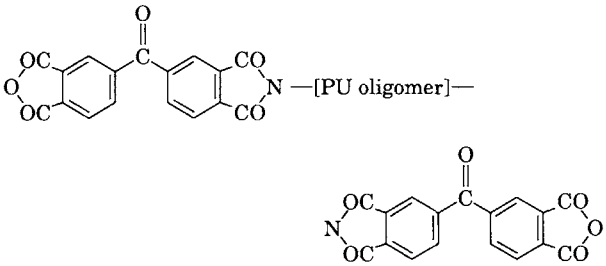


Anhydride-terminated prepolymer (AnTPU)

Preparation of PU-modified Epoxy Resin

To prepare the samples, the PU prepolymers were first dissolved in the epoxy resin at 120°C and prereacted for 30 min. A stoichiometric ratio of the hardener HT976 (diaminodiphenyl sulfone) was then introduced and dissolved by mechanical stirring. Next, the resin was degassed at 140°C in vacuum. The cured cycle was 140°C for 2 h followed by 2 h at 200°C in an oven. The sample descriptions are listed in Table I.

Table I Sample Description

Samples	Coupling Agent	PU Type
E(O)	—	—
H(x)[a]	Bis-A	HTPU
A(x)	DDS	ATPU
An(x)	BTDA	AnTPU

[a] x: PU content.

Characterization Techniques of Cured Resin

A DuPont Instruments 910 dynamic mechanical analysis was used to characterize the cured epoxy resin, using a temperature from −100 to 250°C and a heating rate of 5°C/min under nitrogen. The morphologies of the cured specimens were examined by using transmission electron microscopy (TEM). Specimens were microtomed and stained with osmium tetroxide.

The fracture energy, G_{IC}, was determined using a compact tension (CT) specimen and followed a modified ASTM E399-83 procedure for one crack propagation.[11] The crosshead speed was 1 mm/min for all sample tests. Scanning electron micrographs (SEM) of fracture surfaces were obtained with a microscope (JEOL) after the surfaces were sputter-coated with gold to prevent oxidation.

Epoxy Resin Droplet Debonding

The microbond method was used to determine the shear strength of the Kevlar fiber/resin interface.[12] Test specimens were made by using a paper window technique with the direction of the fiber parallel to the parent bobbin. A drop of resin was applied to the Kevlar fiber, resulting in a formation of an ellipsoid bead which retained its shape after curing.

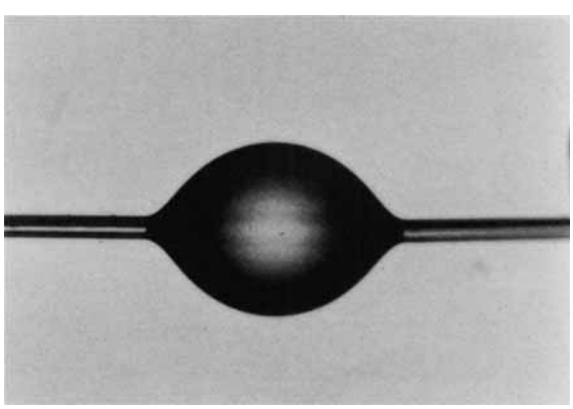


Figure 1 Typical droplet shape of pullout test (×400).

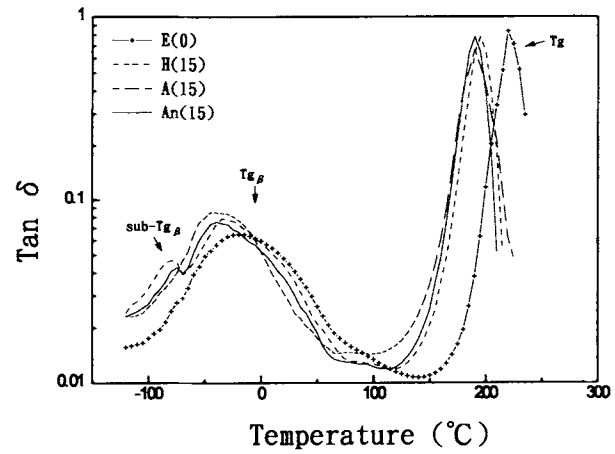


Figure 2 Temperature dependence of tan δ for the PU-modified epoxy.

Once cured, the microdroplet dimension and the fiber diameter were measured by an optical microscope. An example of this typical microdroplet is shown in Figure 1.

For evaluating their interfacial shear strength, the specimen was held in a tensile testing machine in such a way that the fiber end was gripped by the holder and the resin droplet rested between two knife edges. The fiber was then pulled against the knife edges; the load was therefore introduced through the resin droplet.

RESULTS AND DISCUSSION

Dynamic Mechanical Thermal Analysis

The dynamic mechanical thermal behavior of unmodified and PU-modified epoxy resin measured by DMA is shown in Figure 2 and Table II. From the results, it is shown that the peak position of the α-relaxation, which corresponded to the glass transition temperature (T_g) of the cured epoxy resin, was shifted to a lower-temperature region with the increase of PU wt % content as compared to the control system. This suggested that the addition of an excess amount of PU could result in an increase of its micro-Brownian motion of the main chain in the matrix due to the decrease of crosslink density.

From Figure 2, it is also seen that the amine-terminated (ATPU)-modified epoxy resin gave a lower α-relaxation temperature than that of HTPU or AnTPU-modified epoxy. This was believed to be the result of better resin–PU mixing[13] as the DDS coupling agent was used. Therefore, there was an obvious decrease of T_g as the compatibility improved.

Table II Dynamic Glass Transition Temperature of PU-modified Epoxy Network

Sample	T_g α[a] (°C)	T_g β[a] (°C)
E(0)	221	−21
H(5)	218	−26
H(10)	212	−30
H(15)	198	−38
A(5)	214	−32
A(10)	210	−34
A(15)	196	−43
An(5)	215	−29
An(10)	212	−34
An(15)	196	−40

[a] T_g α and T_g β obtained from DMA.

The cured epoxy network was known to have a local transition (T_g, β) in a low-temperature region. It was attributed to vibration of segment chains by the so-called crank shaft mechanism.[14] In the ATPU-modified epoxy resin, the β-relaxation peak of tan δ in M2(15) went toward a lower temperature and became broader as compared to that of the unmodified epoxy resin. Moreover, it did not show the separate transition peak (sub-T_g, β) as seen in other modified resins (HTPU and AnTPU). This demonstrated that the ATPU component in the matrix did not aggregate into a pure rubber phase; instead, the PU phase was mixed with the epoxy resin to form an ATPU-rich domain.

In contrast, with an addition of HTPU or AnTPU, there was a sub-T_g, β relaxation peak, which corresponded to the transition motion of the PU soft segment and which occurred at −78 and −76°C, respectively. This suggested that a clearly two-phase separation existed in the HTPU or AnTPU-modified epoxy system. It was also observed that the magnitude of sub-T_g relaxation peak was very obvious with the increase of PU content and also that the value of the peak in HTPU-modified

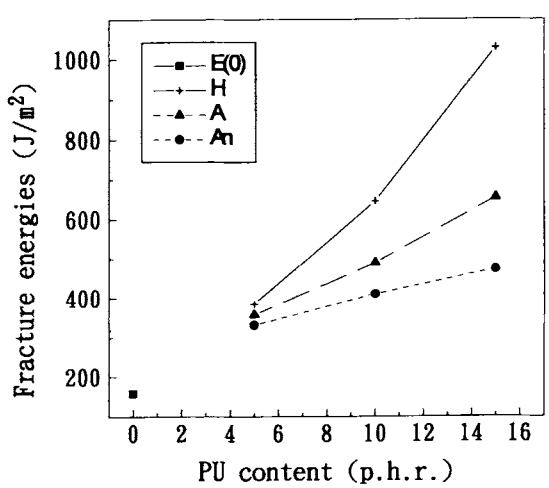


Figure 3 Effect of PU concentration on the fracture energies G_{IC}.

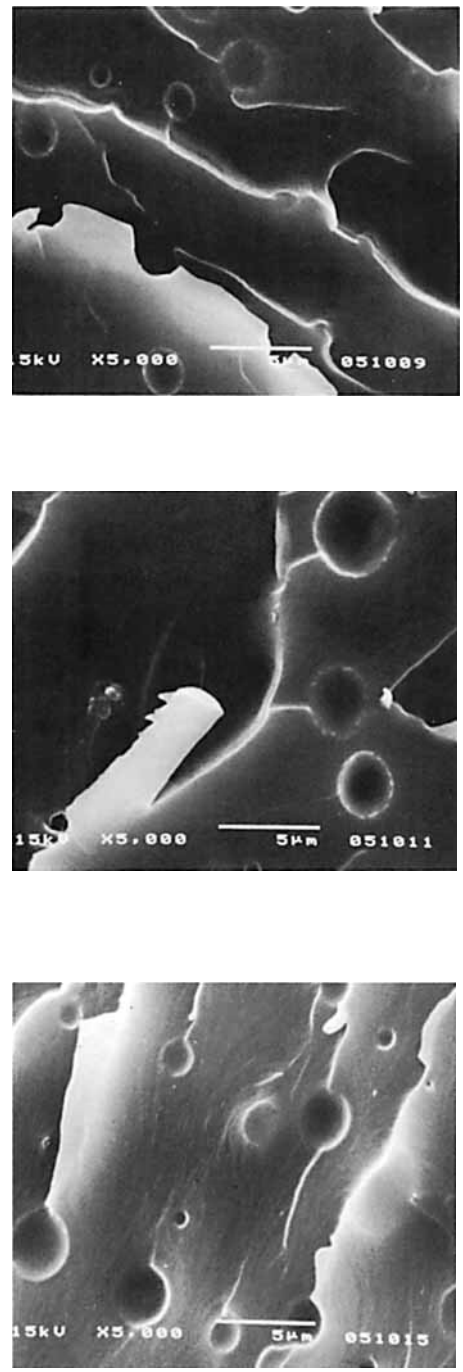


Figure 4 SEM micrographs of the fracture surface of CT specimens: (a) H(10); (b) A(10); (c) An(10).

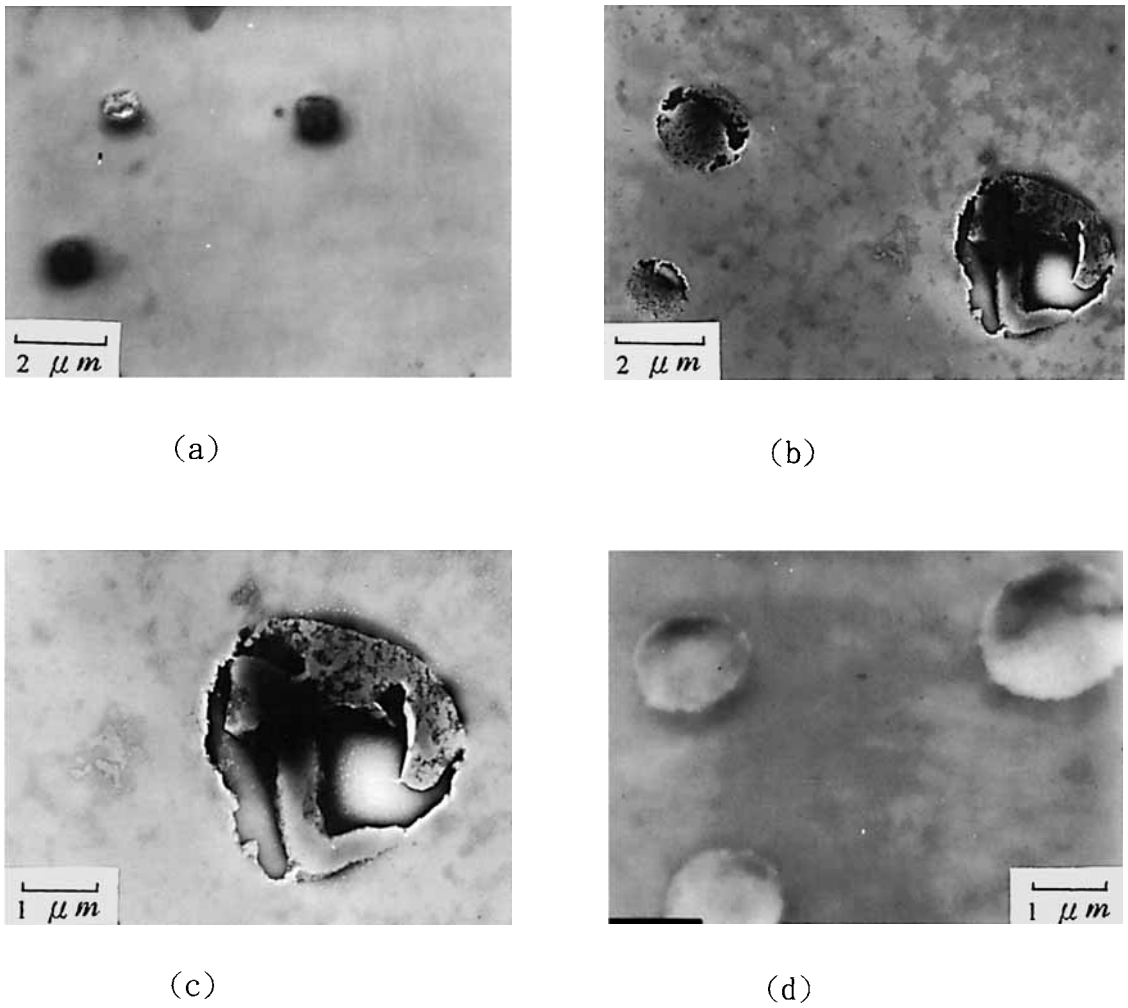


Figure 5 TEM micrograph of OsO_4-stained PU-modified epoxy: (a) H(10); (b, c) A(10); (d) An(10).

epoxy was more pronounced than that in AnTPU-modified epoxy.

Morphologies and Mechanical Characterization

The fracture energies (G_{IC}) of the cured epoxy resin were considerably enhanced by the inclusion of functional PU prepolymers, as seen in Figure 3. Among those three prepolymers, the HTPU was found to be the most effective. It was approximately a fivefold increase in fracture energy than that of unmodified epoxy resin. The increase in these values was believed to be the presence of plastic deformation during fracture.[15,16]

Figure 4(a)–(c) illustrates the effect of PU modifiers on the morphology of fracture surfaces of the CT specimen for the PU-modified epoxy system. A two-phase morphology was apparently present in all samples. The cavities in these micrographs were considered to be the cavitation and fracture of the PU particles. For the HTPU-modified epoxy, the number of these distributed cavity droplets were more than those of the ATPU- or AnTPU-modified epoxy.

Figure 5(a)–(d) shows the transmission electron micrographs (TEM) of the epoxy resins toughened with 10 phr of PU; it was demonstrated that the morphology of the ATPU- and AnTPU-modified epoxies had a dispersed particle with a grain structure. This might indicate that a microgelation could occur during its prereaction of amine- or anhydride-terminated prepolymer. Nevertheless, the morphology of the HTPU-modified epoxy only appeared as dark dispersed particles of the PU-rich phase. This suggested that more phase separation of the HTPU-modified system had occurred.

Figure 6 shows the particle-size distributions for all samples containing 10 phr of the PU modifier.

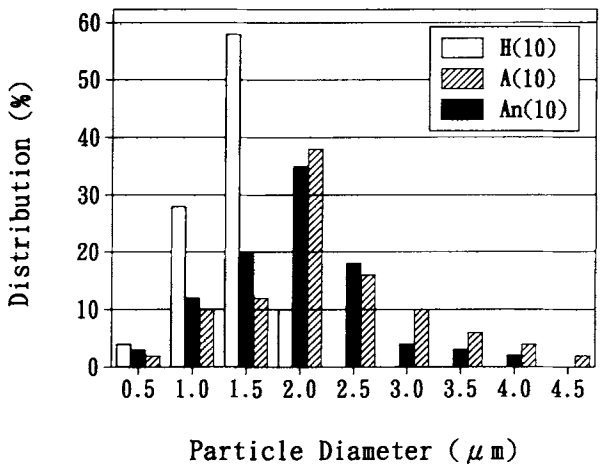


Figure 6 Distribution of PU-particle diameter for PU-modified epoxy with 10 phr PU content.

From the results, it was demonstrated that the ATPU-modified epoxy exhibited a broad particle-size distribution, ranging from 0.5 μm to some above 4.0 μm in diameter. Nevertheless, the HTPU-modified epoxy showed only a uniform distribution of particles with diameters of 1–2 μm. From that, it might be concluded that the hydroxyl group of HTPU in the chain end could form a more linear structure (less crosslink) during its molecular weight buildup by chain extension; therefore, a better improvement of its toughness resulted.

Interfacial Shear Force of Polyaramid Fiber/Epoxy and Fracture Mode

A typical debonding load-interfacial area for the polyaramid fiber/epoxy resin is shown in Figure 7. It was noticeable that a linear relationship between

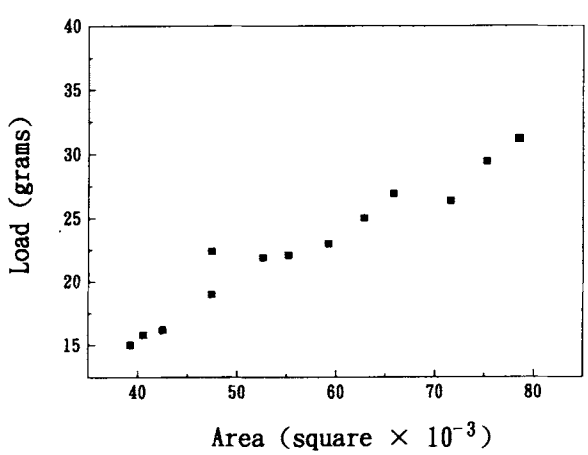


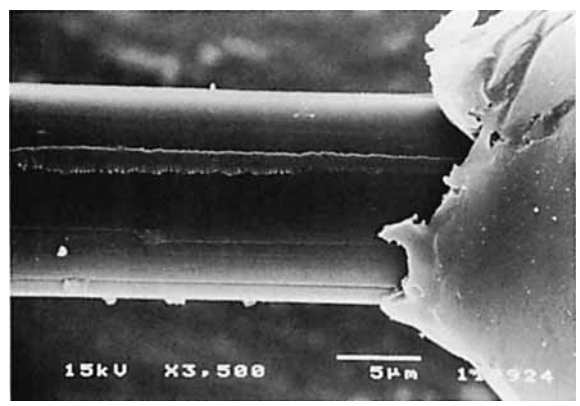
Figure 7 Debonding load vs. embedded area for Kevlar 49/E(0).

Table III Interfacial Shear Strength (τ_s) of Kevlar/Epoxy from Pullout Test

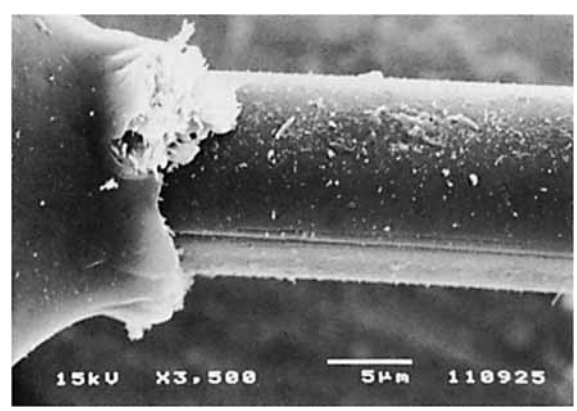
Samples	τ_s (MPa)
E(0)	38.2
H(5)	45.5
H(10)	60.2
H(15)	71.2
A(5)	39.5
A(10)	40.1
A(15)	48.8
An(5)	41.2
An(10)	52.4
An(15)	62.8

load and area existed. For a single-fiber pullout test, the interfacial shear strength τ_s of the bond was determined from the maximum debond load, F, i.e.:

$$\tau_s = \frac{F}{\pi d l}$$



(a)



(b)

Figure 8 SEM micrographs of droplet edge after debonding on fiber: (a) E(0); (b) H(10).

where d is the diameter of the fiber, and l, the embedded length. Table III summarizes the test results of the interfacial shear strength for unmodified and PU-modified epoxy resin on the Kevlar 49 fiber.

From the results, it was found that the strengths of the interfacial bond formed in Kevlar/PU-modified epoxy resins were significantly greater than those in the unmodified epoxy resin. Furthermore, at these levels of fracture energies, the Kevlar/epoxy interface could effectively enhance its energy absorption of debonding. Consequently, the HTPU-modified epoxy could have high fracture energies due to its good interfacial shear strength.

Figure 8(b) shows the scanning electron micrographs of PU-modified epoxy resin after its fiber pullout test; it was found that some polymeric material was still left on the fiber surface. This suggested that an improvement of adhesion within the interfacial layer and a ductile fracture might have occurred. On the contrary, a clean surface of the fiber in the unmodified epoxy is seen in Figure 8(a), indicating that a brittle fracture had occurred. Thus, the existence of this unclean surface as well as its good shear strength in the fiber/resin interface could lead to a cohesive failure in the modified epoxy.

CONCLUSIONS

Epoxies toughened with reactive hydroxyl-, amine-, or anhydride-terminated polyurethane were prepared and studied in terms of their structure—property relationships. Preliminary results indicated that the fracture energy (G_{IC}) of modified epoxy resin and the interfacial shear strength (IFSS) of polyaramid fiber/epoxy were increased with increasing modifier concentration. Among these three prepolymers, the hydroxyl-terminated PU was found to be the most effective.

From the morphological features, a two-phase structure, consisting of spherical PU particles dispersed in the epoxy matrix, was formed. The hydroxyl-terminated PU-modified epoxy exhibited a more uniform distribution of particle diameter. In addition, the existence of an unclean fiber surface after its fiber pullout test suggested that a ductile fracture might have occurred.

From the dynamic mechanical analysis, it was shown that the hydroxyl- and anhydride-terminated modified epoxy resin showed a phase separation peak of the β transition, whereas the β transition of amine-terminated modified epoxy only exhibited a broad distribution, indicating a better miscibility of ATPU with epoxy.

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