

Toughening of Epoxy Resin by Functional-Terminated Polyurethanes and/or Semicrystalline Polymer Powders

HUEI-HSIUNG WANG, JUNG-CHIEH CHEN

Graduate School of Textile Engineering, Feng Chia University, Taichung, Taiwan, Republic of China

Received 2 November 2000; accepted 16 April 2001

ABSTRACT: Hydroxyl-, amine-, and anhydride-terminated polyurethane (PU) prepolymers, which were synthesized from polyether [poly(tetramethylene glycol)] diol, 4,4'-diphenylmethane diisocyanate, and a coupling agent, bisphenol-A (Bis-A), 4,4'-diaminodiphenyl sulphone (DDS), or benzophenonetetracarboxylic dianhydride, were used to modify the toughness of Bis-A diglycidyl ether epoxy resin cured with DDS. Besides the crystalline polymers, poly(butylene terephthalate) (PBT) and poly(hexamethylene adipamide) (nylon 6,6), with particle sizes under 40 μm were employed to further enhance the toughness of PU-modified epoxy at a low particle content. As shown by the experimental results, the modified resin displayed a significant improvement in fracture energy and also its interfacial shear strength with polyaramid fiber. The hydroxyl-terminated PU was the most effective among the three prepolymers. The toughening mechanism is discussed based on the morphological and the dynamic mechanical behavior of the modified epoxy resin. Fractography of the specimen observed by the scanning electron microscopy revealed that the modified resin had a two-phase structure. The fracture properties of PBT-particle-filled epoxy were better than those of nylon 6,6-particle-filled epoxy. Nevertheless, the toughening effect of these crystalline polymer particles was much less efficient than that of PU modification. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2903–2912, 2001

Key words: polyurethanes; epoxy; morphology; interfaces

INTRODUCTION

Epoxy resins were often utilized as the matrix in composite because of their good mechanical properties, high chemical resistance, and excellent dimensional stability. However, their low toughness, especially in the presence of sharp cracks, detracts from their application. Several methods^{1–3} have been proposed to increase the toughness of the epoxy network, and one of the most successful routes has been to incorporate a second phase of dispersed rubbery particles into the

crosslinked network. The primary factor of a rubber-modified matrix is necessary for a chemical linkage of the rubber with the resin. This not only increases the molar mass of the rubber that leads to a phase separation but also ensures intrinsically strong chemical bonds across the rubbery phase/resin matrix interface. Otherwise, a premature failure at the particle–matrix interface, caused by the presence of high-stress concentration at the boundary, will occur.

Moreover, Chiao et al.⁴ indicated that the interlaminar shear and transverse tensile strength of a composite are highly dependent on the toughness of matrix resins and also the properties of fiber/matrix interface, which play an important role in controlling the mechanical properties of

Correspondence to: H.-H. Wang (hhwang@fcums1.fcu.edu.tw).

Journal of Applied Polymer Science, Vol. 82, 2903–2912 (2001)
© 2001 John Wiley & Sons, Inc.

the composite. The surface treatments and coupling agents developed for glass and graphite reinforcements that have been studied increase interfacial strengths by 2×3 times over untreated composites.^{5,6} Unfortunately, similar bonding-promoting methods are not readily available for a polyaramid-reinforced composite system. Consequently, interface-sensitive properties are weaker in polyamide-containing systems than those of their glass or graphite counterparts.^{7,8} Thus, the low off-axis properties of polyaramid-reinforced composites have given rise to numerous investigations aimed at improvement of filament–matrix adhesion.^{9,10} In addition, to avoid the loss of thermal properties, crystalline polymer in powder form has also been used as a second phase^{11–15} to toughen the high-crosslink-density epoxy.

In this study, we attempted to toughen the epoxy network using polyurethane (PU) as the modifier to substantially increase the interfacial shear strength (IFSS) of a polyaramid fiber/epoxy matrix interface. The problem of chemically linking the modifier to the epoxy network was overcome with bisphenol-A (Bis-A), 4,4'-diaminodiphenyl sulphone (DDS), or benzophenone tetracarboxylic dianhydride (BTDA) as a coupling agent between the PU and the epoxy oligomer. Additionally, to further enhance the toughness efficiency, semicrystalline polymers in particle form [poly(butylene terephthalate) (PBT) and nylon 6,6] were blended with the epoxies before curing.

EXPERIMENTAL

Materials

Polytetramethylene glycol (PTMG 2000) was kindly supplied by Evermore Chemical Industry Co. (Taipei, Taiwan). 4,4'-Diphenylmethane diisocyanate (MDI), Bis-A, BTDA, and DDS were purchased from Merck Co. (Darmstadt, Germany). All materials were used as received.

Dimethyl acetamide (DMAc) was first distilled over CaH₂ at 90°C/10 mmHg and then stored in molecular sieves.

The Bis-A diglycidyl ether type epoxy resin (Epon 826) was obtained from Shell Chemical Corp. (Houston, TX) (equivalent weight = 190 g/mol). The hardener diaminodiphenyl sulphone (HT976) was obtained from Ciba-Geigy Corp (Basel, Switzerland).

PBT and nylon 6,6 polymer chips were obtained from Du Pont Co. (Wilmington, DE); these were ground into powder and then sieved to a fine size of 40 μm.

Synthesis of Functional-Terminated PU Prepolymer

The functional-terminated PU prepolymers were prepared by the reaction of 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 reacted with 2 equivalents of 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 is shown in Scheme 1.

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 hardener HT976 was then introduced and dissolved by mechanical stirring. Next, the resin was degassed at 140°C in vacuum. The cure cycle was 140°C for 2 h, followed by 2 h at 200°C in oven. Sample descriptions are listed in Table I.

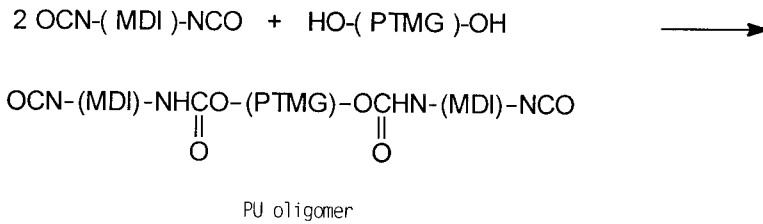
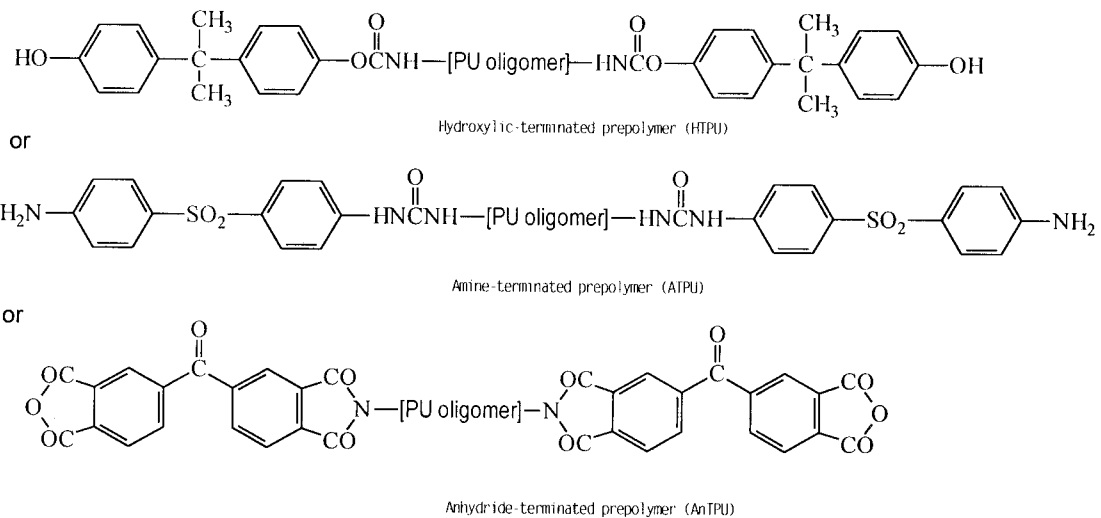
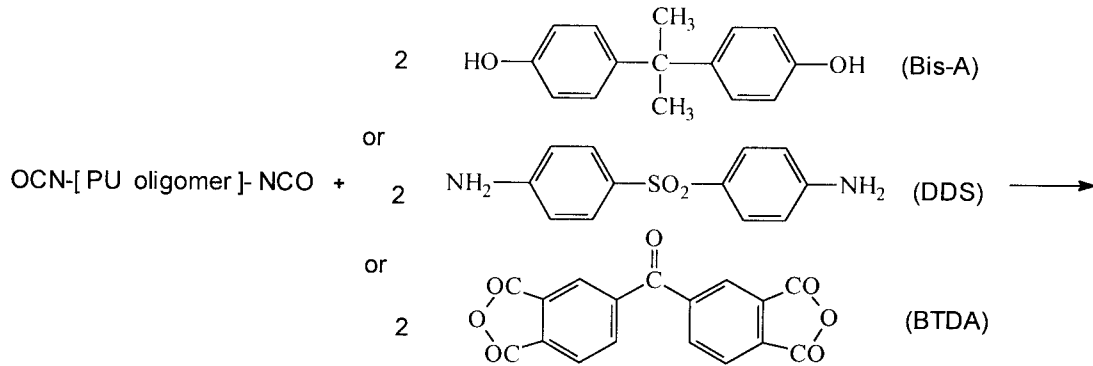
Characterization Techniques of Cured Resin

A DuPont Instruments 910 dynamic mechanical analysis machine (Wilmington, DE) was used to characterize the cured epoxy resin at temperatures from –100 to 250°C, and a heating rate of 5°C/min under nitrogen. IR spectra of the PU prepolymer were recorded by an IR spectrophotometer (Hitachi model 26050, Tokyo, Japan) over a range of 250–4000 cm⁻¹. The film sample was 10 μm thick.

Fracture energy (G_{IC}) was determined with a compact tension (CT) specimen followed a modified ASTM E399-83 procedure for one crack propagation.¹⁶ The crosshead speed was 1 mm/min for all samples tested. Scanning electron microscopy (SEM) micrographs of fracture surfaces were obtained with a microscope (JEOL, Tokyo, Japan) after the surfaces were coated with a vacuum gold sputterer.

Epoxy Resin Droplet Debonding

The microbond method was used to determine the shear strength of the Kevlar fiber/resin inter-

step 1.**step 2.****Preparation of PU-modified epoxy resin****Scheme 1**

face.¹⁷ Test specimens were made with 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, which resulted in the formation of an ellipsoid bead that retained its shape after curing. Once cured, the microdroplet

Table I Sample Descriptions

Sample	Coupling Agent	PU Type
^a E(0)	—	—
H(x) ^a	Bis-A	HTPU
A(x)	DDS	ATPU
An(x)	BTDA	AnTPU

^a x: PU content.

dimension and the fiber diameter were measured with an optical microscope (Olympus, Tokyo, Japan).

For the evaluation of IFSS, specimens were held in a tensile testing machine so 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, and the load was therefore introduced through the resin droplet.

RESULT AND DISCUSSION

Analysis of PU Prepolymers

The IR spectrum of the PU prepolymer is exemplified in Figure 1. The characteristic peaks of the

IR spectrum of the hydroxyl-terminated polyurethane (HTPU) were at 3400 cm^{-1} (—NH— stretch vibration), 1700 cm^{-1} (carbonyl), 2940 cm^{-1} (—CH— stretch vibration), and 1560 cm^{-1} (—NH— deformation). Also, no absorption near 2240 cm^{-1} (—NCO) was observed, indicating the absence of an —NCO group. This indicates that the isocyanate-terminated PU oligomer reacted completely with the Bis-A coupling agent to form a hydrolytic-terminated PU prepolymer.

Dynamic Mechanical Thermal Analysis

The dynamic mechanical thermal behavior of unmodified and PU-modified epoxy resin measured by dynamic mechanical analyzer (DMA) was shown in Figures 2 and 3 and Table II. As shown in Figure 2, the peak position of the glass-transition temperature (T_g) relaxation, which corresponded to the T_g of the cured epoxy resin, shifted to a lower temperature region with the increase of PU weight percent content compared to the control system. This suggests that the addition of an excess amount of PU could result in an increase in the micro-Brownian motion of the main chain in the matrix because of the decrease in crosslink density.

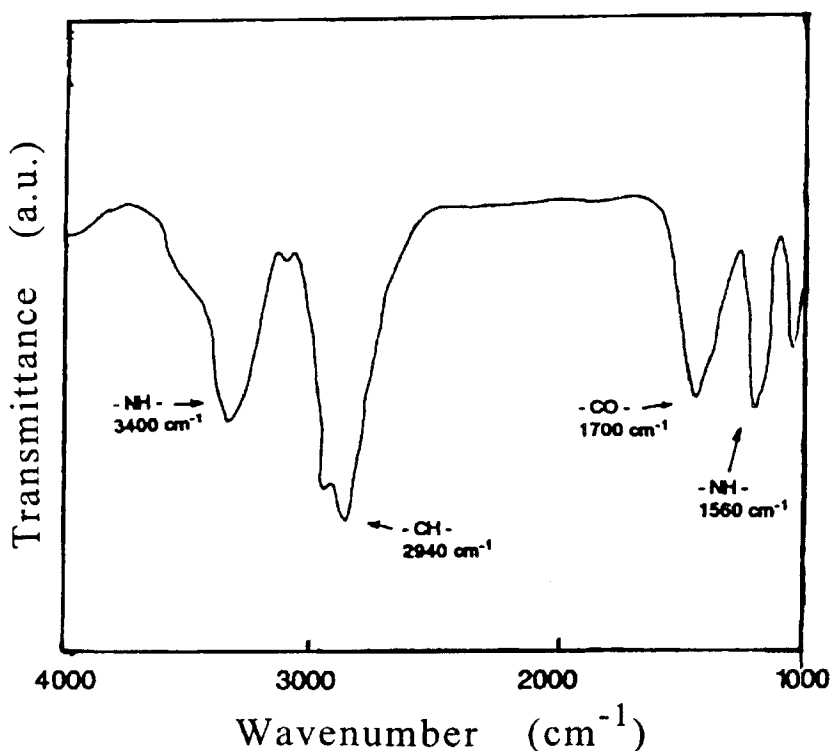


Figure 1 IR spectrum of HTPU-modified PU prepolymer.

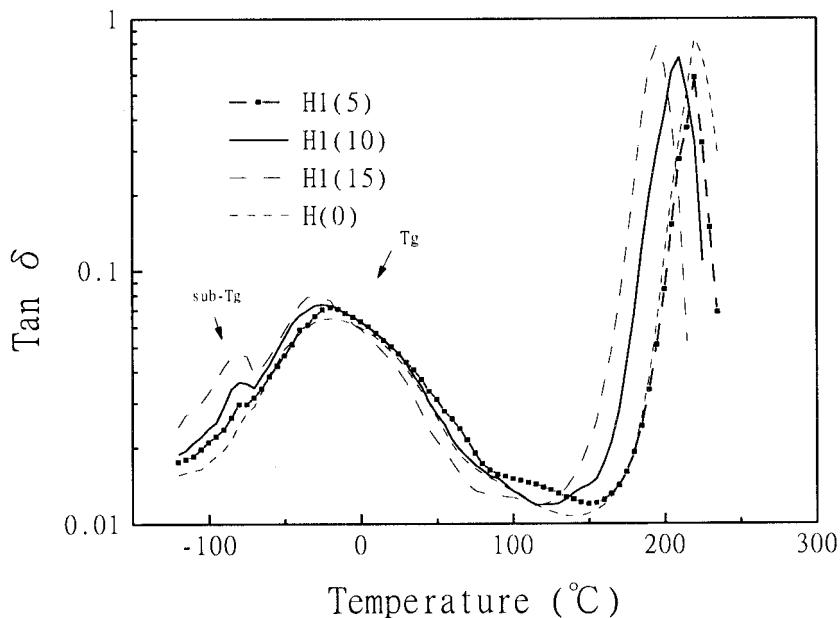


Figure 2 Temperature dependence of $\tan \delta$ for various PU-modified contents.

As shown Figure 3, the amine-terminated polyurethane (ATPU)-modified epoxy resin gave a lower T_g relaxation temperature than those of HTPU- or anhydride-terminated polyurethane (AnTPU)-modified epoxy. This was believed to be the result of better resin-PU mixing,¹⁸ as the DDS coupling agent was used. Therefore, there

was an obvious decrease in T_g as the compatibility improved.

The cured epoxy network is known to have a local transition ($T_{g\beta}$, β) in a low temperature region. This is attributed to vibration of segment chains by the so-called crank-shaft mechanism.¹⁹ In the ATPU-modified epoxy resin, the β relax-

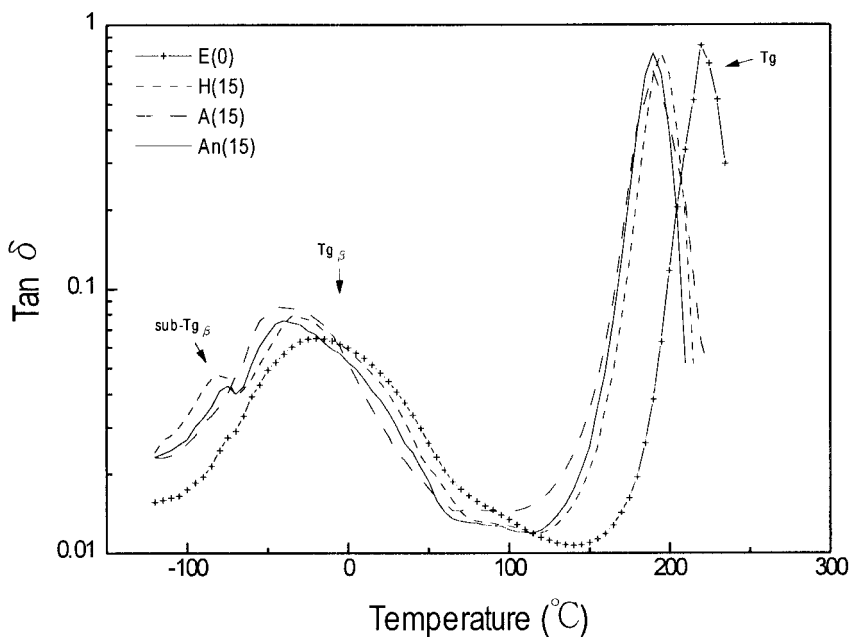


Figure 3 Temperature dependence of $\tan \delta$ for various PU-modified epoxies.

Table II Dynamic T_g of PU-Modified Epoxy Network

Sample	$T_{g\alpha}$ ($^{\circ}\text{C}$) ^a	$T_{g\beta}$ ($^{\circ}\text{C}$) ^a
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 $T_{g\alpha}$, $T_{g\beta}$ obtained from DMA; $T_{g\alpha}$ is the T_g at the hard segment of epoxy region; the $T_{g\beta}$ is the T_g at the soft segment of the PU region.

ation peak of $\tan \delta$ in A(15) went toward a lower temperature and became broader compared to that of the unmodified epoxy resin. Moreover, it did not show the separate transition peak (β' relaxation) as seen in other modified resins (HTPU and AnTPU). This demonstrated that the ATPU component in 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 the addition of HTPU or AnTPU, there was a β' relaxation peak that corresponded to the transition motion of the PU soft segment, which occurred at -78 and -76°C , respectively. This suggested that a clear two-phase separation existed in the HTPU- and AnTPU-modified epoxy systems. It was also observed that the magnitude of the β' relaxation peak was much more obvious with the increase of PU content, and also, the value of the peak in the HTPU-modified epoxy was more pronounced than that in the AnTPU-modified epoxy.

Table III T_g of PU-Modified Epoxy Resin with Crystalline Polymer Particles

Crystalline Polymer Content (phr)	T_g ($^{\circ}\text{C}$)				
	0 phr PU	5 phr PU	10 phr PU	15 phr PU	
PBT	0	221.4	218.2	210.1	198.9
	5	221.4	218.0	208.9	196.5
	15	220.5	216.5	205.9	191.1
Nylon 6,6	5	221.3	216.8	206.9	195.5
	15	219.2	214.2	205.1	190.8

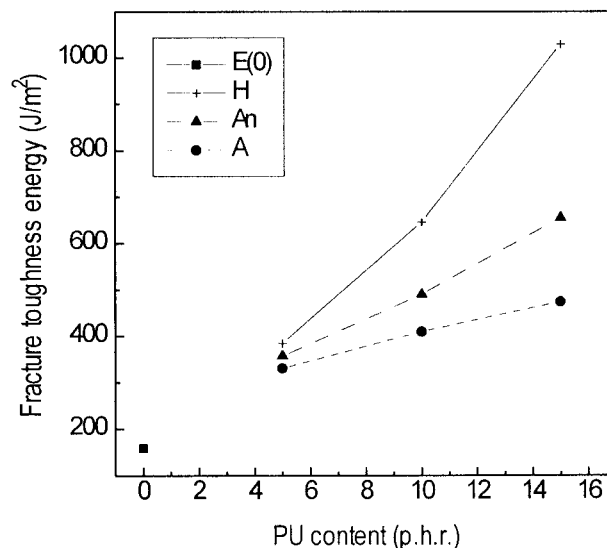
**Figure 4** Effect of PU prepolymers on the G_{IC} of PU-modified epoxy.

Table III summarizes the T_g data of the crystalline polymer-filled PU-unmodified and PU-modified epoxy resins. From the results, the T_g of the unmodified epoxy was not affected by the addition of PBT or nylon 6,6 particles. However, the T_g of the PU-modified epoxy network decreased slightly with the content of PBT or nylon 6,6 particles. This slight decrement of T_g might indicate that the existence of crystalline polymer might have interfered with the curing reaction of the modified epoxies and, therefore, lowered their T_g 's.

Morphologies and Mechanical Characterization

G_{IC} 's of the cured epoxy resin were considerably enhanced by the inclusion of functional PU prepolymers, as seen in Figure 4. Among those three prepolymers, HTPU was the most effective. There was an approximately five-fold increase in G_{IC}

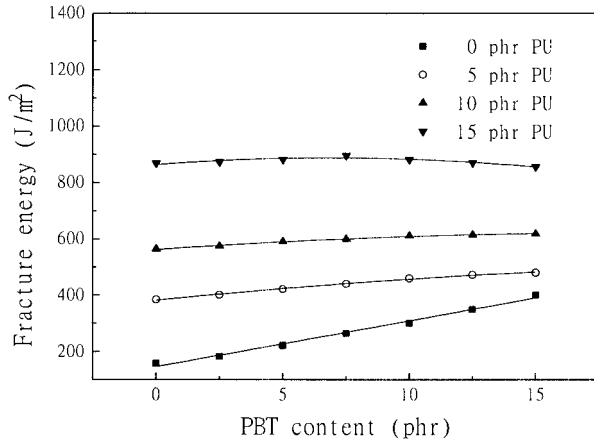


Figure 5 Effect of PBT content on the G_{IC} of PU-modified epoxy.

compared to the unmodified epoxy resin. The increase in these values was believed to be caused by the presence of plastic deformation during fracture.^{20–26}

Figure 5 shows the change of G_{IC} of the PBT-filled epoxy resins with the PBT concentration at 20°C. Evidently, the G_{IC} of the PU-unmodified epoxy network was enhanced by the PBT particles. The toughening mechanism of the crystalline-polymer-toughened network polymer arises from a phase transformation of the crystalline polymer in the front of the crack tip, as described by several authors.⁸ In addition, the effect of PBT filler in the PU-modified epoxy network on the toughness was less efficient than that of the PBT-filled unmodified epoxy. At high content [15 parts per hundred resin (phr)] of PU-modified epoxy,

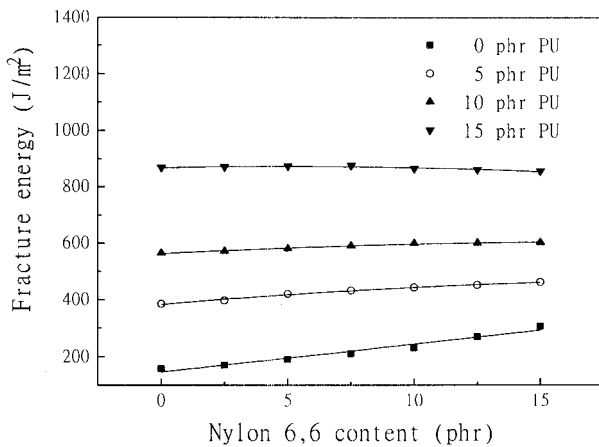
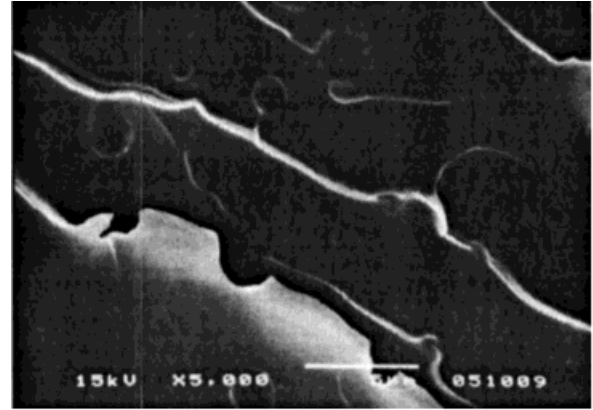
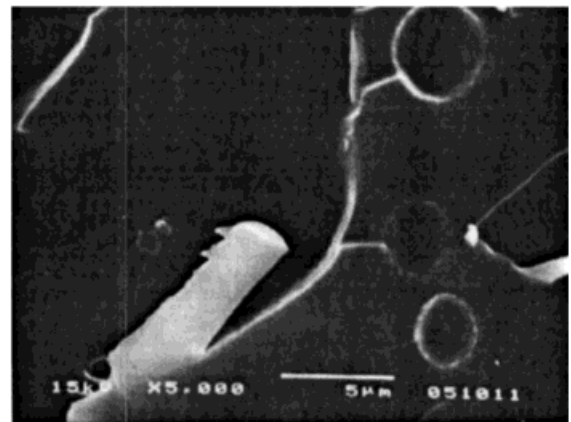


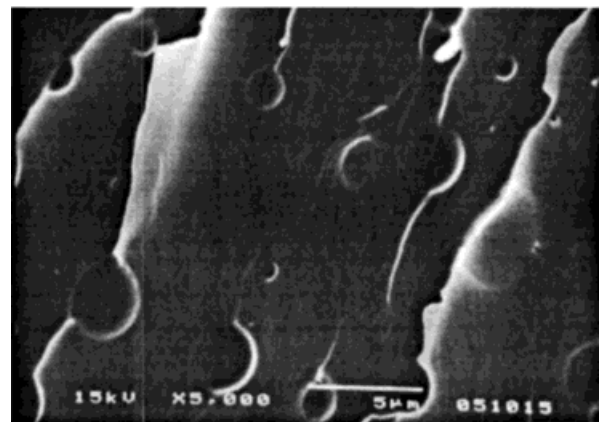
Figure 6 Effect of nylon 6,6 content on the G_{IC} of PU-modified epoxy.



(a)



(b)



(c)

Figure 7 SEM micrographs of the fracture surface of CT specimens: (a) H(10), (b) A(10), and (c) An(10).

the G_{IC} decreased with the content of PBT. This could be explained as follows: as the PBT content increased, the plastic deformation of PU domains

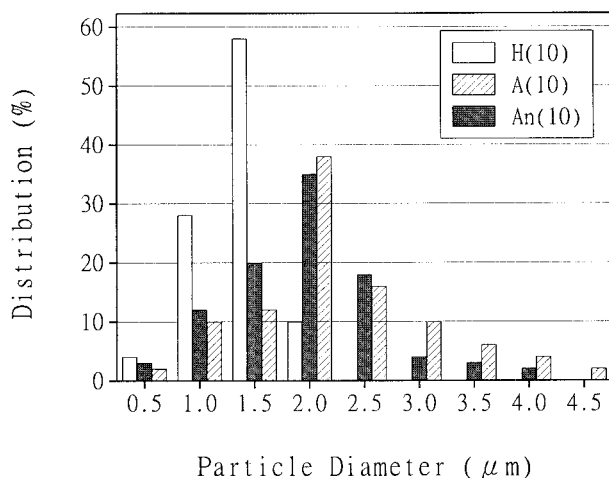


Figure 8 Distribution of PU particle diameter for PU-modified epoxy with 10 phr PU content.

became more restricted; hence, the G_{IC} decreased accordingly.

As shown in Figure 6, the G_{IC} of the unmodified epoxy with 15 phr of nylon 6,6 increased from 190 to 285 J/m². Nevertheless, the addition of PBT was more effective in the enhancement of the G_{IC} of the epoxy network than that of the nylon 6,6.

Figure 7(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 apparent 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.

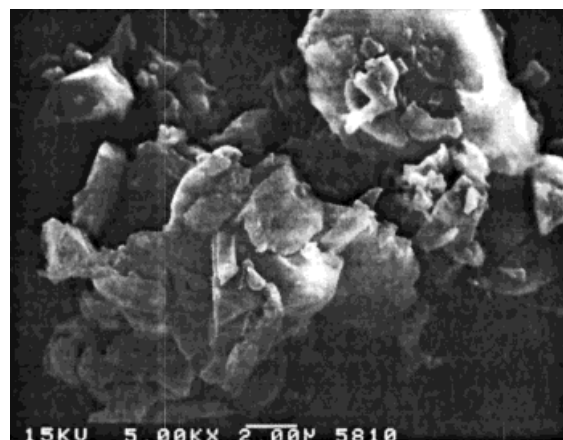
Figure 8 shows the particle-size distributions for all samples containing 10 phr of PU modifier. The results demonstrate that the ATPU-modified epoxy exhibited a broad particle-size distribution, ranging from 0.5 to some above 4.0 μm in diameter. Nevertheless, the HTPU-modified epoxy only showed a uniform 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 have formed a more linear structure (fewer crosslinks) during its molecular weight buildup by chain extension; therefore, a better improvement of its toughness resulted.

Figure 9 (a,b) shows SEM micrographs of the postfailure appearance of CT specimens of PBT and nylon 6,6-filled PU-modified epoxy, respectively. As shown, the small PBT particles agglomerated into a cluster, and the crack passed be-

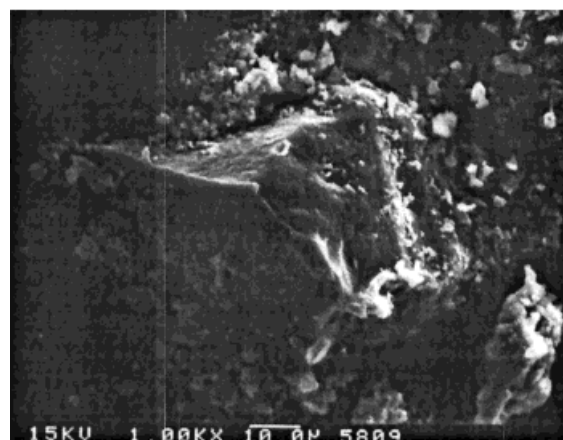
tween these small particles. The cavitation size of the PU cluster seemed to decrease slightly with the addition of crystalline polymer particles. Nevertheless, the toughening effect of the crystalline polymer particles was much less efficient than that of the PU modification.

Interfacial Shear Force of Polyaramid Fiber/Epoxy and Fracture Mode

The typical debonding load–interfacial area for the polyaramid fiber/epoxy resin is shown in Figure 10. A linear relationship was noticeable between load and area. For a single-fiber pull-out test, the IFSS (τ_s) of the bond was determined from the maximum debond load, F , that is



(a)



(b)

Figure 9 SEM micrograph of the fracture surface of CT specimen of (a) PBT-filled and (b) nylon 6,6-filled modified epoxy with 10 phr PU epoxy.

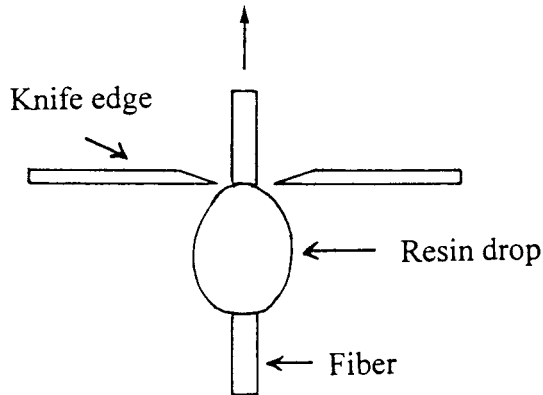


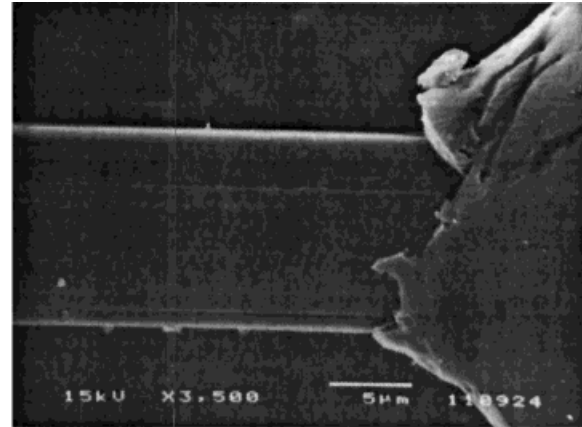
Figure 10 Debonding load test for Kevlar 49/E(0).

$$\tau_s = \frac{F}{\pi dl}$$

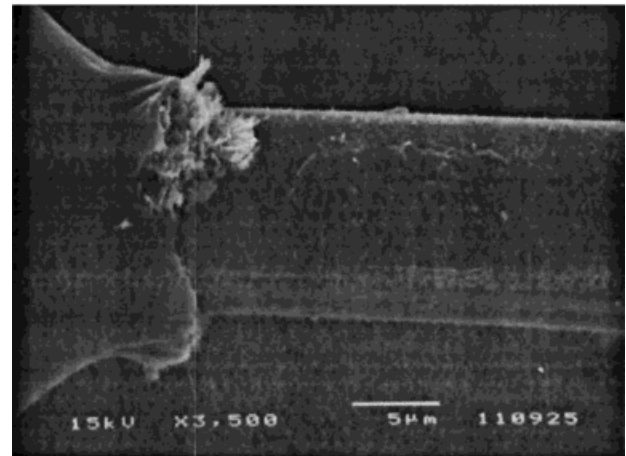
where d is the diameter of the fiber and l is the embedded length.

Table IV summarizes the test results of IFSS for unmodified and PU-modified epoxy resin on the Kevlar 49 fiber. As shown by the results, the strengths of the interfacial bond formed in the 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 effectively enhanced its energy absorption of debonding. Consequently, the HTPU-modified epoxy could demonstrate high fracture energies because of its good IFSS.

Figure 11(a) shows the SEM micrographs of the PU-modified epoxy resin after the fiber pull-out test; some polymeric material was still left on the fiber surface. This suggests that an improve-



(a) E(0)



(b) H(10)

Figure 11 SEM micrographs of droplet edge after debonding on fiber: (a) E(0) and (b) H(10).

Table IV IFSS of Unmodified and PU-Modified Epoxy Resin on the Kevlar 49 Fiber

Sample	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

ment of adhesion within the interfacial layer and a cohesive-type failure might have occurred. On the contrary, a clean surface of fiber in the unmodified epoxy was seen, as shown in Figure 11(b). This indicates a brittle fracture happened. Thus, the existence of this unclean surface and its good shear strength in the fiber/resin interface could have led to a cohesive failure in the modified epoxy.

CONCLUSIONS

Epoxies toughened with reactive HTPU, ATPU, or AnTPU were prepared and studied in terms of their structure–property relationships. Prelimi-

nary results indicate that the G_{IC} of modified epoxy resins and IFSS of polyaramid fiber/epoxy increased with increasing modifier concentration. Among these three prepolymers, HTPU was the most effective.

From the morphological features, a two-phase structure, consisting of spherical PU particles dispersed in the epoxy matrix, was formed. The HTPU-modified epoxy exhibited a more uniform distribution of particle diameter. In addition, the existence of an unclean fiber surface after a fiber pull-out test suggested that a cohesive-type failure might have occurred.

Dynamic mechanical analysis showed in the HTPU- and AnTPU-modified epoxy resins the presence of a phase-separation peak of β relaxation, whereas the β relaxation of ATPU-modified epoxy only exhibited a broad distribution, indicating a better miscibility of ATPU with epoxy.

For thermal properties, the PU-modified epoxy exhibited a lower T_g than the unmodified epoxy. The T_g decreased with PU content. However, the addition of crystalline polymer particles did not greatly affect the thermal properties of the PU-modified epoxy.

REFERENCES

- Hwang, J. F.; Manson, J. A.; Hertzberg, R. W.; Miller, G. A.; Sperling, L. H. *Polym Eng Sci* 1989, 29, 1466.
- Kinloch, A. J.; Shaw, S. J.; Tod, D. A.; Hunston, D. L. *Polymer* 1983, 24, 1341.
- Bennett, G. S.; Farris, R. J.; Thompson, S. A. *Polymer* 1991, 32, 1633.
- Chiao, C. C.; Moore, R. L.; Chiao, T. T. *Composite* 1977, 8, 161.
- Bajaj, P.; Jha, N. K.; Kumar, A. *J Appl Polym Sci* 1992, 44, 1921.
- Moon, C. K.; Lee, J. O.; Cho, H. H.; Kim, K. S. *J Appl Polym Sci* 1992, 45, 443.
- Allred, R. E.; Roylance, D. K. *J Mater Sci* 1983, 18, 652.
- Allred, R. E. *National SAMPE Symp* 1984, 29, 947.
- Penn, L. S.; Bystry, F. A.; Machionni, H. J. *Polym Compos* 1983, 4, 26.
- Wertheimer, M. R.; Schreiber, H. P. *J Appl Polym Sci* 1981, 26, 2087.
- Kim, J. K.; Robertson, R. E. *J Mater Sci* 1992, 27, 161.
- Kim, J.; Robertson, R. E. *J Mater Sci* 1992, 27, 3000.
- Nichols, M. E.; Roberston, R. E. *J Mater Sci* 1994, 29, 5916.
- Xiao, H. X.; Frisch, K. C.; Frisch, H. L. *J Polym Sci Polym Chem Ed* 1983, 21, 2547.
- Kim, D. S.; Cho, K.; An, J. H.; Park, C. E. *J Mater Sci Lett* 1992, 11, 1197.
- Bucknall, C. B.; Partridge, I. K. *Brit Polym J* 1983, 15, 71.
- Miller, B.; Mrui, P.; Rebenfeld, L. *Compos Sci Technol* 1987, 28, 17.
- Bates, F. S.; Cohen, R. E.; Argon, A. S. *Macromolecules* 1983, 16, 1108.
- Kline, D. E. *J Polym Sci* 1960, 47, 237.
- Garg, A. C.; Mai, Y. W. *Compos Sci Technol* 1988, 31, 179.
- Sue, H. J. *Polym Eng Sci* 1991, 31, 275.
- Frisch, H. L.; Wang, L.; Huang, W.; Hua, Y. H. *J Appl Polym Sci* 1991, 43, 475.
- Truong, V. T.; Truong, Y. B.; Ennis, B. C. *Polym Commun* 1991, 32(9), 275.
- Vakil, U. M.; Martin, G. C. *J Appl Polym Sci* 1992, 46, 2089.
- Cheng, C.; Hiltner, A.; Baer, E.; Soskey, P. R.; Mylonakis, S. G. *J Mater Sci* 1995, 30, 587.
- Sunil, K. N.; Golok, B. N. *J Adhes Sci Technol* 1993, 7, 105.