

Glycidyl-Terminated Polyurethane Modified Epoxy Resins: Mechanical Properties, Adhesion Properties, and Morphology

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SYNOPSIS

Glycidol was used to convert the isocyanate-terminated polyurethane prepolymer to glycidyl-terminated polyurethane prepolymer. The modified polyurethane not only offers some distinct advantages over the commercial polyurethane prepolymer, but also enhances the properties of the epoxy resins. The glycidyl-terminated polyurethane modified epoxy resin proved to be superior to conventional epoxy resins in improving impact strength, fracture energy, and adhesion properties. The compatibility of the compounds in this glycidyl-terminated PU/epoxy system was investigated using different preparation procedures. It was found that the synthesized glycidyl-terminated polyurethane prereacted with curing agents, exhibited a lesser degree of phase separation, and can influence the mechanical properties of polymer blends. The results coincide with the phenomena observed in dynamic mechanical analysis and scanning electron microscopy. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It is known that epoxy resins have high glass-transition temperatures (T_g), are rigid and brittle in nature, and have poor crack resistance.¹⁻³ In order to overcome these problems, a considerable amount of study has been done in the direction of toughening epoxies, with some research focused on introducing a rubber phase into epoxy networks.⁴⁻⁷ Polyurethane resin possesses high impact strength and exhibits excellent low-temperature performance.^{8,9} This study is based on a blending technique, introducing a second reactive polyurethane polymer into the epoxy resins, to make up for the deficiencies of the existing material.

Although polyurethane resins possess excellent low temperature properties, chemical and environmental resistance, and high impact properties, com-

mercial polyurethanes contain free isocyanate groups, which lead to some limitations.¹⁰⁻¹¹ Small amounts of moisture will interfere with proper curing, which limits the amount of materials used to comparatively large quantities. Another class of compound is that in which the isocyanate groups are "blocked" or "capped" with an "active hydrogen" compound.¹²⁻¹³ These products show little or no reaction at room temperature. Some of the disadvantages of employing blocked isocyanates are that a high temperature or a long period of time are required for unblocking, as well as the difficulty in removing the blocking agents during the process.

In the previous study,¹⁴ a modified polyurethane was prepared which could overcome these disadvantages. Glycidol was used to transfer the isocyanate-terminated polyurethane prepolymers to glycidyl-terminated polyurethane prepolymers. Crosslinking in these cases occurs primarily through the epoxide groups, and the modified system offers some distinct advantages over the commercial polyurethane resins, for example, good storage stability and room temperature curing.

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Polymer blends encompass many different kinds of materials containing two or more polymer components; the most important parameter that affects the properties of polymer blends is the degree of phase separation. There are several factors that control the degree of phase separation. These factors include the compatibility of the polymers, the molecular diffusion, and the synthetic environment, such as the reaction procedures and reaction temperature.¹⁵⁻¹⁷ In the present work, the effect of the different preparation procedures on phase separation and the relationship between the mechanical properties, dynamic mechanical behavior, compatibility, and morphology of the glycidyl-terminated PU/Epoxy system were investigated.

EXPERIMENTAL

Materials

The materials used in this study are described in Table I. Glycidyl-terminated polyurethane prepolymer was synthesized in this research. The polyol (PPG-2000) was heated at 60°C and was degassed by vacuum overnight before use. The TDI, glycidol, epoxy resin, and crosslinking agents were employed as received.

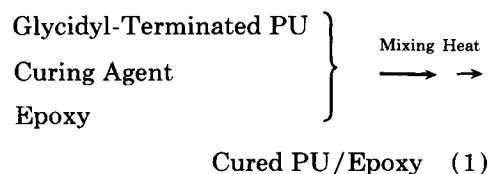
Preparation of Glycidyl-Terminated Polyurethane Resins

The preparation of glycidyl-terminated polyurethane resin was carried out in two steps. An isocyanate-terminated polyurethane prepolymer was synthesized in the first step. The glycidol was then added to the prepolymer and was reacted with the NCO groups through hydroxy groups, hence the prepolymer will be glycidyl-terminated. Experimental details are described elsewhere.¹⁴

Preparation of Glycidyl-Terminated PU/Epoxy Sample

Two types of glycidyl-terminated PU/epoxy sample were prepared, as illustrated below:

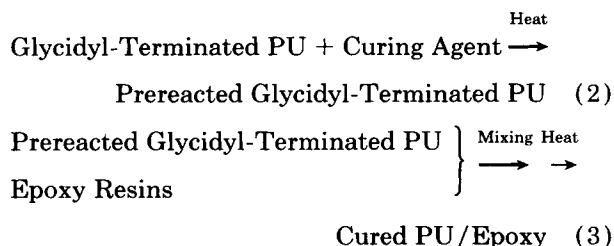
Simultaneous Technique



One equivalent of epoxy resin, with various contents of glycidyl-terminated polyurethane and amine curing agent, as shown in Table II, were mixed homogeneously using a high torque stirrer.

After mechanical agitation and degassing for 30 min, the mixture was cast in a stainless steel mold at 100°C for 2 h. Finally, it was further heated to 120°C and was kept at this temperature for another 6 h. Upon removal from the mold, samples were kept in a desiccator and were maintained at 50% R.H., for at least 3 days before they were tested.

Prereacted Technique



Glycidyl-terminated PU was prereacted with all the amine curing agents at 100°C under a stream of nitrogen. A sample of reacting mixture was taken every half hour for IR analysis and was determined by the HBr titration method (ASTM D-1652) separately. The absorption peak for epoxy groups ($\sim 915 \text{ cm}^{-1}$) decreased during the reaction and eventually disappeared. The results indicated that

Table I Materials Used in this Study

Designation	Description	Source
PPG-2000	Poly(Propylene Oxide) Glycol, $MW = 2000$	Chiung Long Co., Taiwan, ROC
TDI	Toluene Diisocyanate	BASF, Germany
DER-331	Epoxy Resin, $EEW = 188$	Dow Chemical Co., USA
D-230	Polyoxypropyleneamines	Jefferson Chemical Co., USA
Glycidol	2,3-epoxy-1-propanol	Aldrich Co., USA

Table II Formulations of the Glycidyl-Terminated PU/Epoxy Materials

Component	Glycidyl-Terminated PU Content (phr)					
	0	5	10	15	20	25
Epoxy Resin (DER-331) ^a (gm)	407.4	392.4	378.2	365.1	352.9	341.4
Glycidyl-terminated PU ^b (gm)	0	19.6	37.8	54.7	70.6	85.4
Curing Agent (D-230) (gm)	142.6	138.0	134.0	130.2	126.5	123.2

^a Epoxide equivalent of DER-331 is 188.

^b Epoxide equivalent of synthesized glycidyl-terminated PU is 1956.

the epoxy groups in the glycidyl-terminated PU reacted with the $-NH_2$ group of the amine curing agent completely.

When the first step was finished, the prereacted glycidyl-terminated PU and epoxy resins were mixed homogeneously. The mixture was cast in a stainless steel mold at 100°C for 2 h and was heated further to 120°C for another 6 h. The sample was then demolded and was maintained at 50% R.H. in a desiccator for at least 3 days before testing.

Testing Methods

IR spectra were recorded on a Domet DA3-002 FT-IR spectrometer to detect the absorption peaks, which were characteristic of the resins during the synthetic procedures.

The epoxide equivalent of glycidyl-terminated polyurethanes was determined by titrating with a standard solution of HBr in acetic acid following the procedure described in ASTM D-1652.

The tensile properties were measured on an Instron 4201 universal test unit. The tensile properties were determined, as described in ASTM D-638, with a crosshead speed of 1 cm/min. Five specimens were tested for each sample.

The flexural properties were measured by an Instron 4201 universal material testing machine. The flexural strengths were tested following ASTM D-790. The sample dimensions were $12.7 \times 1.27 \times 0.2$ cm, the span was 9 cm, and the crosshead speed was 2 mm/min. Five specimens were tested for each sample.

The impact strengths were measured by an impact tester, TMI No. 43-01 (Testing Machines Inc. USA). The Izod impact strengths were measured according to ASTM D-256. The impact value was determined by averaging the values of 8–10 specimens.

The tensile shear strength properties were measured on an Instron 4201 universal test unit. The

test specimens used were made of 6016-T6 aluminum alloy. The surfaces to be bonded were etched by the sodium dichromate-sulfuric acid etching process.¹⁸ The glycidyl-terminated PU/epoxy mixtures were then applied to the metal within 30 min. The test specimens were bonded together under a pressure of 100 psi and were cured for seven days at room temperature. The cured glue line thickness was controlled at 0.003 ± 0.0005 inch. The test procedures at room temperature and low temperature followed the methods described in ASTM D-1002 and ASTM D-2557, respectively.

DSC was carried out on a Dupont 990 thermal analyzer. All thermograms were baseline corrected, were normalized to sample weight, and were calibrated by using indium and sapphire. The scan rates employed were 5°C/min.

The dynamic mechanical properties of the specimens were measured using a Rheometrics dynamic spectrometer, Model RDS-7700, over a temperature range of -120°C to 70°C , at a heating rate of 5°C/min, and at a frequency of 1 Hz. The dimensions of the sample were approximately $6 \times 1 \times 0.2$ cm.

SEM was taken for the fractured surface of the fracture energy test specimen at liquid nitrogen temperature with a Hitachi S-570 instrument.

The fracture energy, G_{Ic} , was measured using compact-tension specimens (CTS).¹⁹ The G_{Ic} value was calculated as follows:

$$G_{Ic} = \frac{Y^2(a/w)P^2a}{EW^2b^2}$$

Where $Y(a/w) = 29.6 - 186(a/w) + 656(a/w)^2 - 1017(a/w)^3 + 639(a/w)^4$. Here a , b , and E are crack length, thickness, and modulus, respectively, of the specimen, and P is the load on the specimen. A sharp precrack was made with a razor blade before the test. The specimens were tested on a screw-driven Instron machine at a crosshead rate

of 0.5 cm/min. The G_{Ic} value was determined by averaging the values of 6–8 specimens.

The fracture energy was measured according to ASTM E813-89. The J -integral method was used to estimate the fracture toughness of material near the initiation of slow stable crack growth. For “multiple specimen technique,” several specimens were prepared, each specimen was cut with a diamond knife, and was knocked with a sharp razor blade, which was immersed in liquid nitrogen, and was then compression tested using an Instron 4201 tester with a span-to-width ratio, S/W , set at 4 and a crosshead speed of 0.5 mm/min.²⁰ With different extensions, each sample had a different stress whitening zone and different input energy. The J value can be calculated by the following equation.²¹

$$J = 2U/Bb$$

where U is the input energy of the specimen, which is the area below the load-displacement curve, B is the thickness of the specimen, and b is the ligament length. The J_{Ic} value is the intersection of the regression line of each experiment and the blunting line.

$$J_{Ic} = 2\sigma_y\Delta a$$

where σ_y is the tensile yield stress and Δa is the length of stress whitening zone.

RESULTS AND DISCUSSION

Mechanical and Adhesion Properties

The mechanical properties of the glycidyl-terminated PU/epoxy, with various glycidyl-terminated PU contents, are shown in Table III. Figure 1 shows the notched Izod impact strength (i.e., high shear rate fracturing) of the glycidyl-terminated PU/epoxy with various glycidyl-terminated PU contents. From Table III and Figure 1, it can be seen that the notched Izod impact strength of glycidyl-terminated PU/epoxy increased with PU content. When the glycidyl-terminated PU added is 15 phr, the notched izod impact strength was increased more than 200% (from 14.9 J/M to 33.1 J/M). This behavior is attributed to the introduction of the glycidyl-terminated PU soft segment into epoxy matrix, which toughens the matrix.

Figures 2 and 3 show the flexural strength, flexural modulus, tensile strength, and tensile modulus of the glycidyl-terminated PU/epoxy at various polyurethane contents. The mechanical properties of glycidyl-terminated PU/epoxy showed no improvement and slightly decreased with the glycidyl-terminated PU content. The results coincide with the theory that S. S. Labana described.²² Crosslinking density may affect the physical properties. Improvements are most significant above the glass transition temperature. For example, a modulus, measured below the glass transition temperature, changes slightly, whereas the modulus decreases, with a decreasing degree of crosslinking, above the glass transition. In this system, glycidyl-terminated

Table III Mechanical Properties of Glycidyl-Terminated PU/Epoxy at Various Glycidyl-Terminated PU Contents

Property	Glycidyl-Terminated PU Content (phr)							
	0	5	10	15	20	25		
Notched izod impact strength (J/M)	14.9 ± 0.2	22.0 ± 1.1	26.0 ± 1.3	33.1 ± 1.9	35.4 ± 2.2	38.0 ± 2.3		
Tensile strength (MPa)	60.2 ± 0.5	59.5 ± 0.3	56.6 ± 1.7	52.7 ± 0.2	48.4 ± 0.7	46.1 ± 0.3		
Flexural strength (MPa)	103.2 ± 0.7	99.8 ± 1.0	94.0 ± 1.5	88.2 ± 1.3	82.1 ± 1.6	73.9 ± 2.0		
Tensile modulus (MPa)	2160 ± 114	2212 ± 23	2065 ± 36	2015 ± 127	1811 ± 118	1699 ± 132		
Flexural modulus (MPa)	2529 ± 28	2468 ± 14	2265 ± 55	2196 ± 60	1996 ± 40	1893 ± 23		

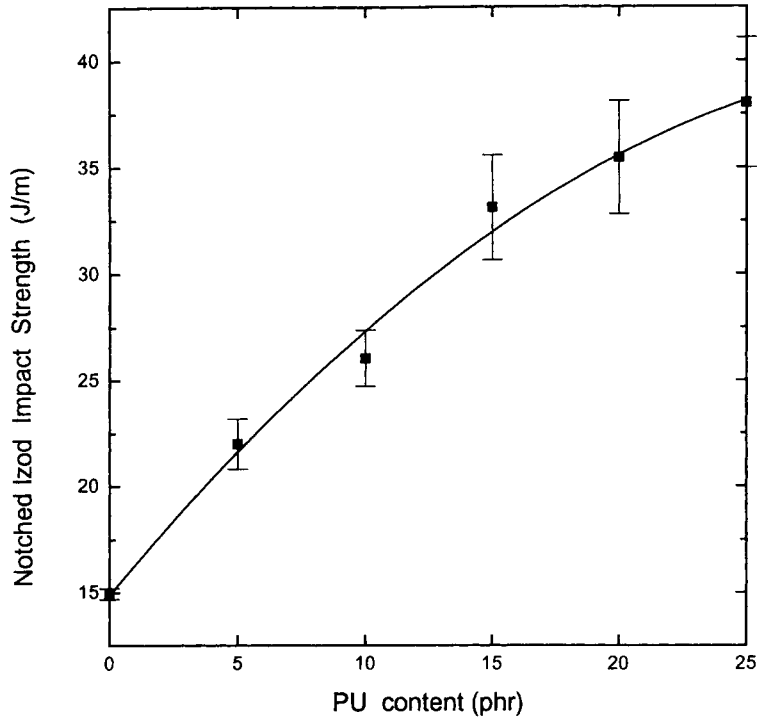


Figure 1 Effect of glycidyl-terminated polyurethane content on the notched Izod impact strength of glycidyl-terminated PU/epoxy.

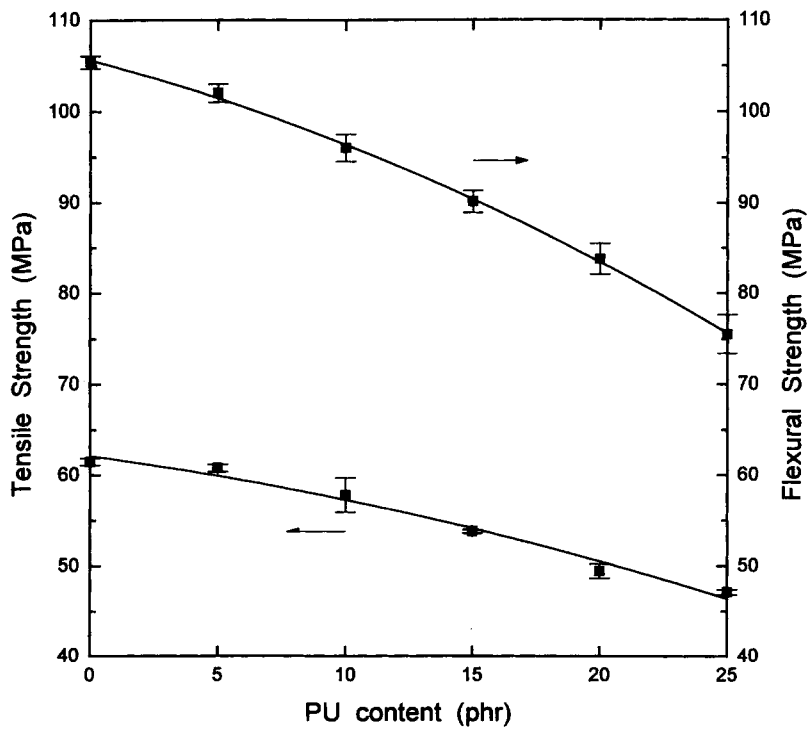


Figure 2 Effect of glycidyl-terminated polyurethane content on the tensile strength and flexural strength of glycidyl-terminated PU/epoxy.

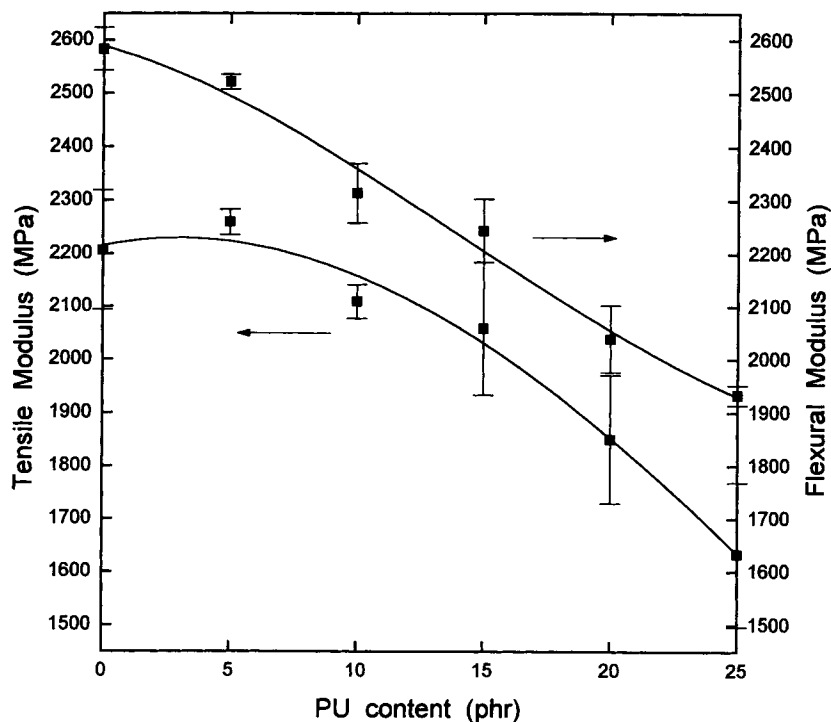


Figure 3 Effect of glycidyl-terminated polyurethane content on the tensile modulus and flexural modulus of glycidyl-terminated PU/epoxy.

PU and epoxy resin have the same terminal group (i.e., epoxide group), and the molecular weight of the glycidyl-terminated PU (M.W. \approx 3900) is larger than that of the epoxy resin (e.g., M.W of DER331 is about 376). Figure 4 shows the different topology of cured epoxy resin and glycidyl-terminated PU/epoxy mixture. From Figure 4, it can be seen that the glycidyl-terminated PU-modified epoxy resins have lower crosslinking densities than the virgin system and, consequently, both tensile strength and flexural strength were decreased. Tensile modulus and flexural modulus of the glycidyl-terminated PU/epoxy decreased with PU content as well.

The adhesion properties of the glycidyl-terminated PU/epoxy are shown in Table IV. The modified system exhibits higher tensile shear strength than the epoxy resin at cryogenic temperatures, with a slight increase at room temperature with the glycidyl-terminated PU content. The polyurethane type adhesives were found to possess the highest tensile and peel strengths at cryogenic temperature. The above results are attributed to the degree of flexibility of the soft segment structures in polyurethanes.²³⁻²⁵

One of the important features of these modified systems is that the glycidyl-terminated polyurethane significantly improves both the adhesion property

at cryogenic temperature and the impact strength of epoxy resins, although with decreases in the other mechanical properties. In general, elastomers or "toughening" agents, added to the base polymer, may cause a serious loss in tensile strength, modulus, and flexural strength.²⁶ This trade-off can be lessened by the use of certain elastomers that react *in situ* during epoxy crosslinking.⁷ In the present study, it was found that, although there are no rubber particles in the matrix, the notched Izod impact strength and the adhesion properties at cryogenic temperature and room temperature could be improved by chemically modifying epoxy resin with glycidyl-terminated polyurethane.

Fracture Energy

The fracture energy (i.e., low shear rate fracturing) was measured by using either the G_{Ic} or the J_{Ic} method. The G_{Ic} method is suitable for the linear elastic fracture mechanism (LEFM) analysis,²⁷ that is, brittle type failure specimens can be analyzed by the G_{Ic} method. On the other hand, the J_{Ic} method is suitable for elastic-plastic fracture mechanistic (EPFM) analysis,²⁸ that is, ductile type failure specimens can be analyzed by the J_{Ic} method. The fracture energy of the glycidyl-terminated PU/

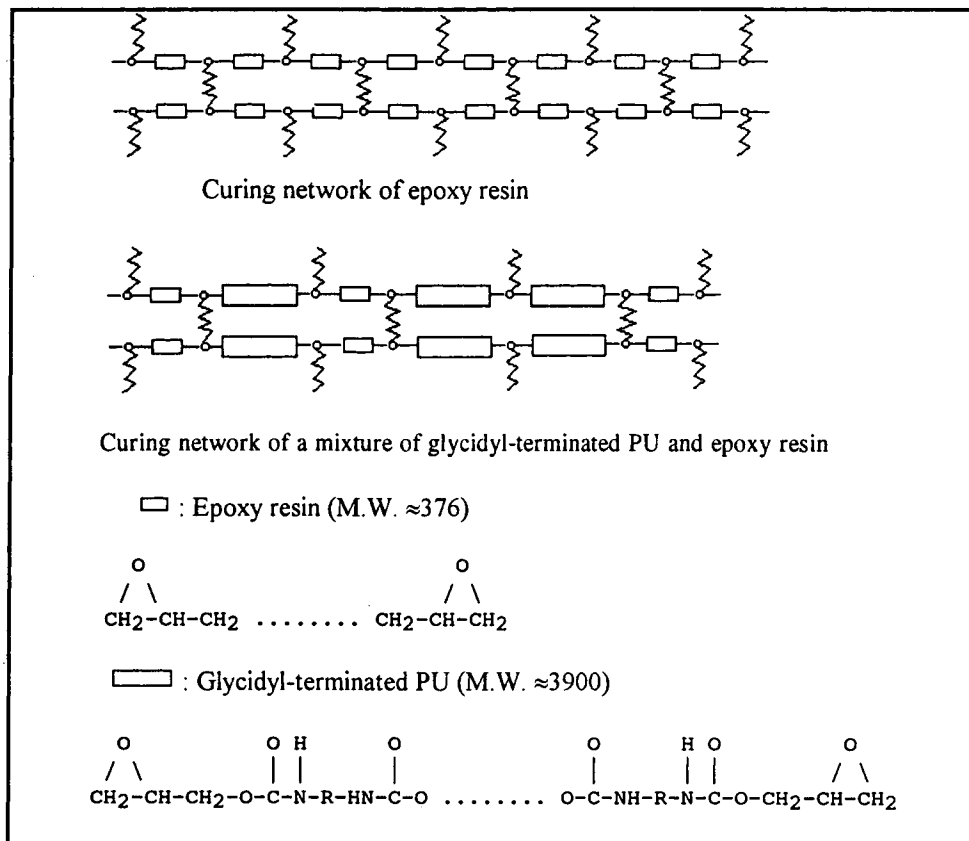


Figure 4 Schematic representation of basic structure and curing network of epoxy resin and glycidyl-terminated PU/epoxy blend system.

Table IV Tensile Shear Strength Data of Glycidyl-Terminated PU/Epoxy at Various Glycidyl-Terminated PU Contents

Glycidyl-Terminated PU Content (Phr)	Tensile Shear Strength of Modified Epoxy on Aluminum, psi (MPa)	
	-320°F (-160°C)	77°F (25°C)
0	960 ± 25 (6.6 ± 0.2)	2160 ± 150 (14.9 ± 1.0)
5	1435 ± 70 (9.9 ± 0.5)	2183 ± 95 (15.0 ± 0.7)
10	1935 ± 45 (13.3 ± 0.3)	2235 ± 130 (15.4 ± 0.9)
15	2100 ± 120 (14.5 ± 0.8)	2270 ± 145 (15.7 ± 1.0)
20	2150 ± 105 (14.8 ± 0.7)	2256 ± 152 (15.5 ± 1.1)
25	2400 ± 135 (16.6 ± 0.9)	2330 ± 125 (16.1 ± 0.9)

epoxy, with various glycidyl-terminated PU contents, is illustrated in Figure 5 and Table V. The virgin systems of epoxy resins are somewhat brittle in nature and are reflected in their stress/strain behavior, such as epoxy resin (DER331), cured with polyoxypropyleneamine (D-230) in this study, which shows fracture in the linear elastic mode.²⁹ Their fracture energies are denoted as G_{Ic} . The fracture behaviour of the epoxy, with PU content below 5 phr, is similar to the unmodified system. When the glycidyl-terminated PU added is 10 phr, the specimen is too ductile to be measured by the G_{Ic} method, since the load-deflection relations deviate from linearity. Meanwhile, the specimen is too brittle for J_{Ic} analysis, due to the quickly propagating crack under testing, which results in only a little stress whitening zone at the front of the specimen and a featureless zone at the rear part of the specimen. For these reasons, the specimen with 10 phr PU cannot be analyzed by either the G_{Ic} or the J_{Ic} method. When the glycidyl-terminated PU content is more than 10 phr, all these specimens show the bulk nonlinear, nonelastic behavior, hence, the J

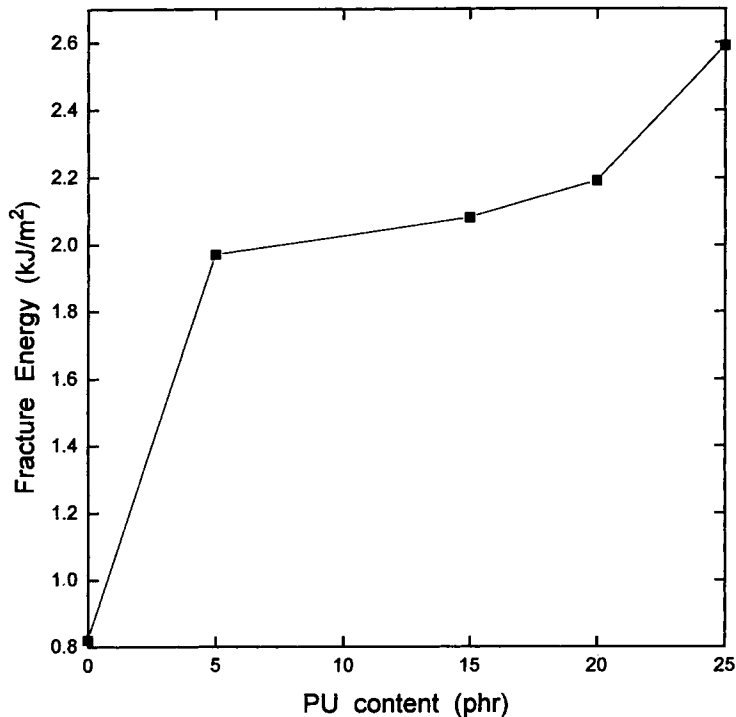


Figure 5 Effect of glycidyl-terminated polyurethane contents on the fracture energy of glycidyl-terminated PU/epoxy.

contour integral method was employed to present the fracture energy.³⁰ Figure 6 illustrates the plot of *J* vs. crack extension and, consequently, the *J_{IC}* value can be calculated.

As shown in Figure 5 and Table V, the fracture energy of the glycidyl-terminated PU/epoxy increased with increasing PU content in the system. This behavior was due to the presence of PU soft segments in the epoxy matrix, which would increase the flow behavior of molecular chains in typical ductile tearing. Meanwhile, the reaction between glycidyl-terminated PU and curing agent decreases the crosslinking density of the system that would increase the ability of the molecular chain to deform by shear yielding. Both contributions show the synergistic effect on the fracture energy of the glycidyl-terminated PU/epoxy samples. The fracture mechanism of these specimens will be discussed in detail with the morphology of the fracture surfaces.

Morphologies

Toughened plastics, such as the glycidyl-terminated PU/epoxy, are simply attributed to delaying or retarding the crack initiation and allowing the pre-crack plastic zone to grow over its critical value. Figure 7 shows the observation of fracture surfaces

of glycidyl-terminated PU/epoxy with various glycidyl-terminated PU contents. From these photographs, it can be seen that different morphologies exist in these specimens. The fracture surface of unmodified epoxy resin [Figures 7(a) and 8(a)] shows some flat and river patterns in the position of crack initiation. These patterns show that the crack propagates quickly and that there is no stress whitening zone in the crack plane that is similar to typical brittle materials. Figures 7(b) and 8(b) show that

Table V Fracture Energy of Glycidyl-Terminated PU/Epoxy at Various Glycidyl-Terminated PU Contents

Property	Glycidyl-Terminated PU Content (phr)					
	0 ^a	5 ^a	10 ^b	15 ^c	20 ^c	25 ^c
Fracture energy (KJ/m ²)	0.82	2.04	—	2.08	2.19	2.59

^a These data were calculated by the *G_{IC}*'s method for their brittle type of fracture.

^b The specimen represent ductile–brittle transition, so the data are not suitable for either the *G_{IC}*'s or the *J_{IC}*'s analysis.

^c These data were calculated by the *J_{IC}*'s method for their ductile type of fracture.

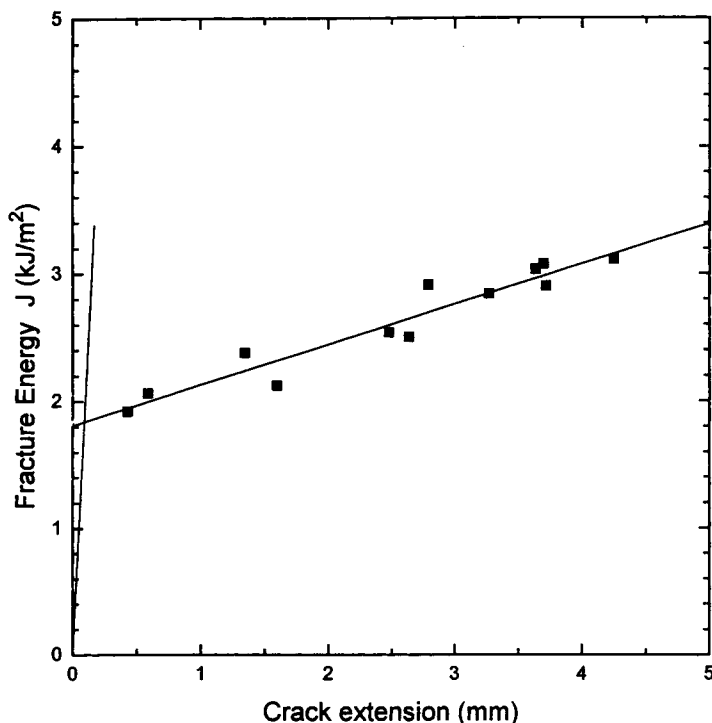


Figure 6 Fracture energy, J , vs. crack extension according ASTM E813-89.

the fracture behavior of the specimen with 5 phr PU is similar to the brittle fracture described for unmodified epoxy resin. However, a narrow stress whitening zone appeared and the fracture energy increased, as compared with the unmodified system. (from 0.82 KJ/m^2 to 2.04 KJ/m^2).

Figures 7(c) and 8(c) are photographs of the fracture surface for the specimen with 10 phr PU. The specimen shows little stress whitening (ductile fracture) at the front of the crack tip and a featureless zone (brittle fracture) at the rear of the specimen. Its fracture behavior show a transition from brittleness to ductility. From the viewpoint of the fracture mechanism, this phenomena can be explained as follows.^{31,32} At first, the stress concentrates at the tip of the crack, thus the incorporation of a soft segment will promote the local yield of the material before the crack propagation. The crack tip plastic zone then blunts the crack, makes a stress whitening zone, and releases the concentration of stress. Meanwhile, the storage energy at the crack tip becomes larger, and finally this energy releases to support the propagation of the crack. The storage energy is high enough to support the crack in passing through the original crack tip stress whitening zone, and to let the crack pass through the entire specimen quickly. Additional evidence to confirm the transition is extant in the appearance of a clear lateral

constriction around the crack tip (as shown in Fig. 9). This phenomenon is consistent with typical ductile fracture.

From Figures 7(d-f), it can be seen that the stress whitening zone occurs throughout the surface when the resin system contains more than 15 phr of the glycidyl-terminated PU. This result can be understood as ductile tearing; there is a larger crack tip plastic zone formed and the storage energy is not large enough to let the crack pass through the plastic zone and, consequently, the crack ceases to propagate and a new plastic zone is formed continuously in the fracture process. Figure 10(a) shows the fracture surface at higher magnification for the SEM microscopic features of the stress whitening zone for a specimen that contains 10 phr glycidyl-terminated PU. The well-defined striated surface, with distorted and irregular marks, is obvious, with the density of striated lines decreasing with increasing PU content [Figs. 10(b) and (c)]. The phenomena are similar to the fractured surfaces of ductile polycarbonate, as Chang et al.^{33,34} described.

Effect of Preparation Procedures on Phase Separation

Glycidyl-terminated PU/epoxy resin can be prepared by the "simultaneous" technique. Simulta-

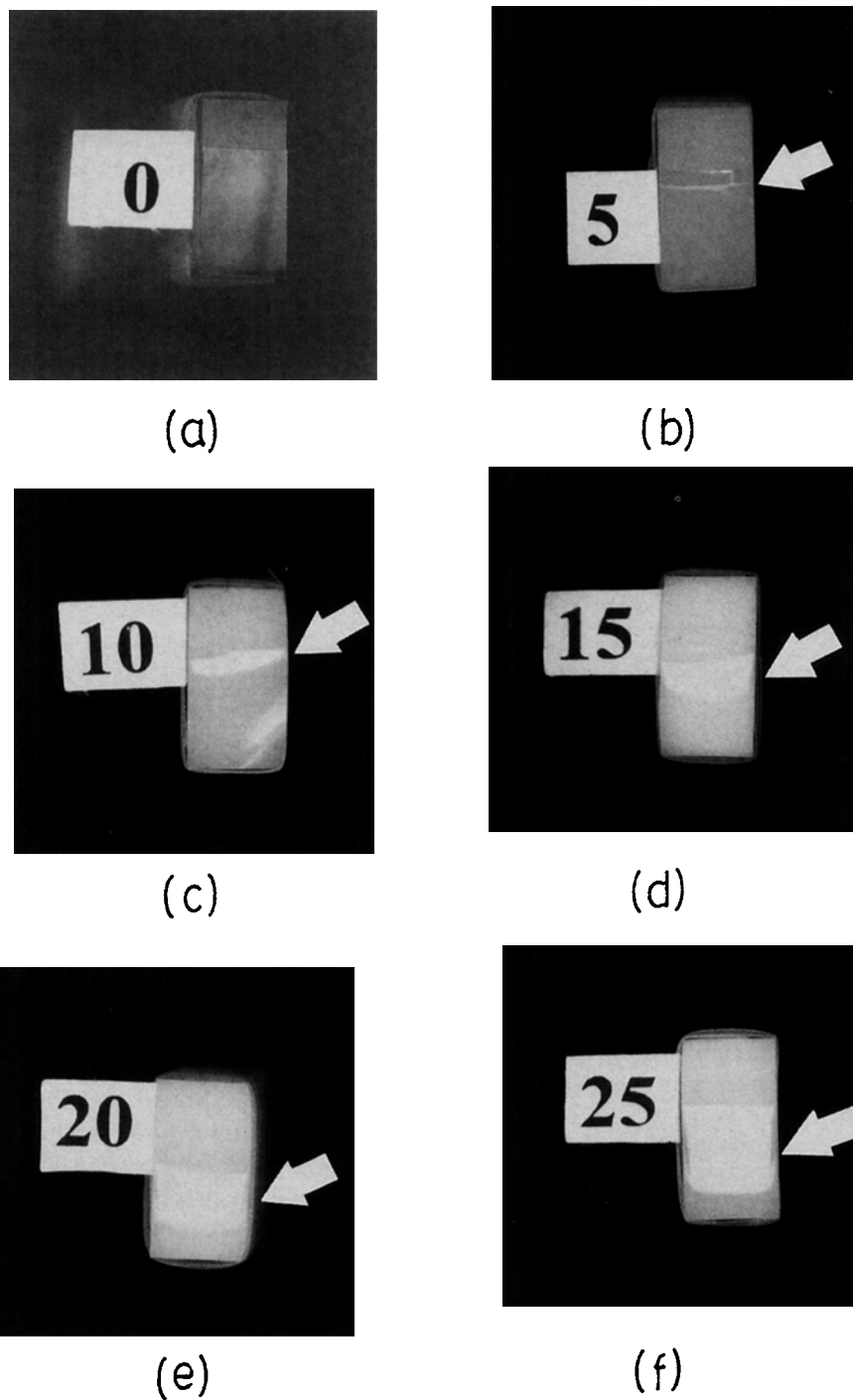


Figure 7 Optical surface view of whitened region of fracture energy test specimen of glycidyl-terminated PU/epoxy with various glycidyl-terminated PU contents. (\Leftarrow) stress whitening zone.

neous curing refers to the mixing of synthesized glycidyl-terminated PU, epoxy resins, and cross-linking agents, cured *in situ* while being molded or cast in the plate. The advantage of the “simultaneous” technique is in the ease of processing.

The synthesized, glycidyl-terminated polyurethane and the epoxy resins have the same terminal group (i.e., epoxy group). These materials are able to react in the network of glycidyl-terminated PU/epoxy. The morphology of a copolymer can be de-

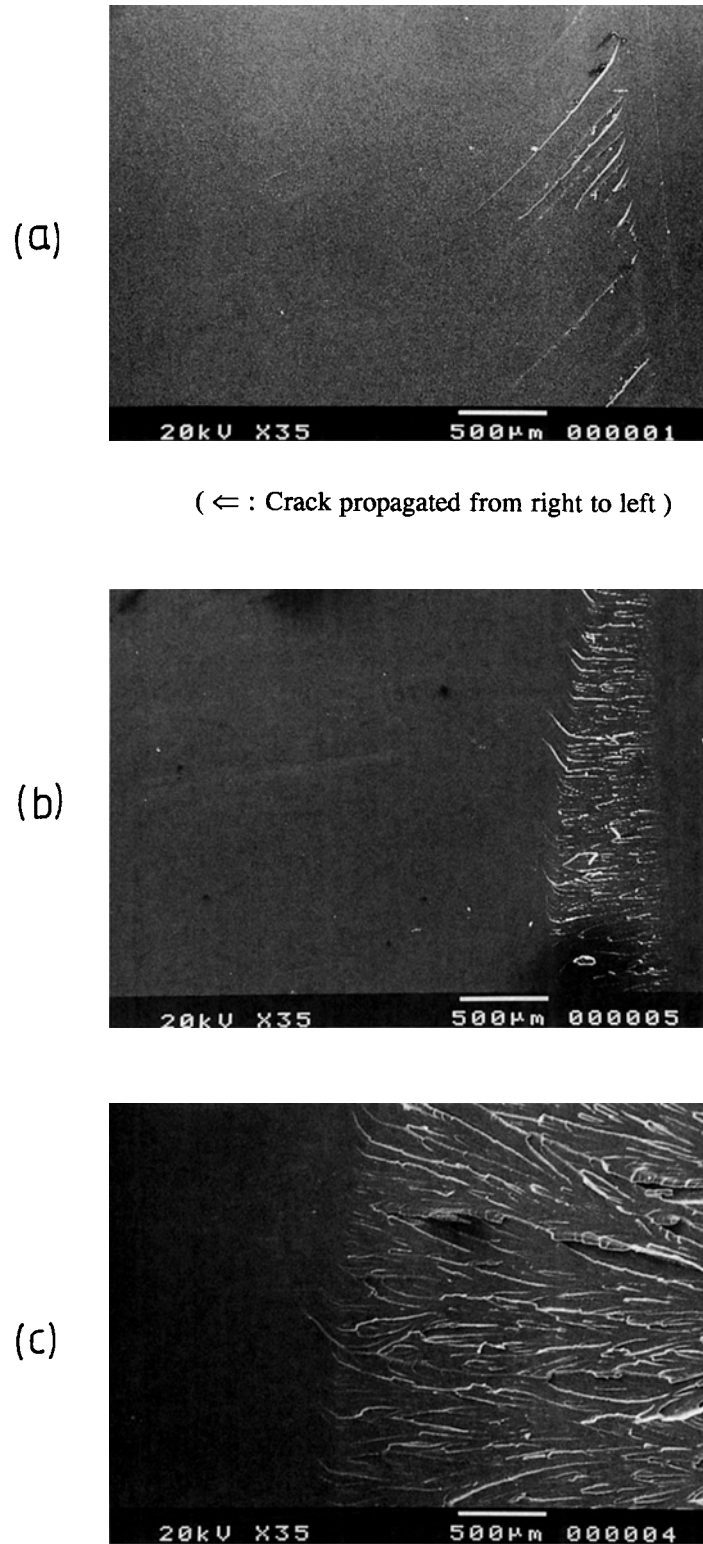
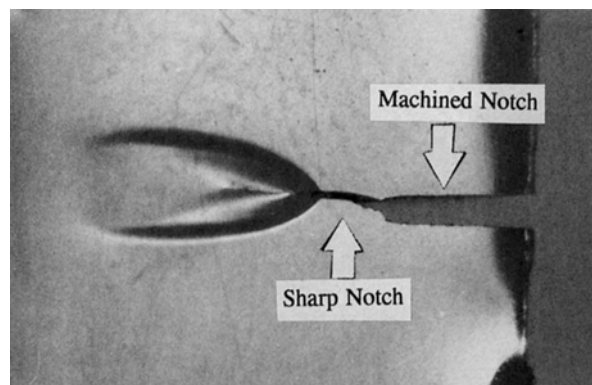


Figure 8 Scanning electron micrograph of the fracture surface of fracture energy test specimen of glycidyl-terminated PU/epoxy with various glycidyl-terminated PU contents. (a) unmodified epoxy resin, (b) 5 phr glycidyl-terminated PU/epoxy blend, and (c) 10 phr glycidyl-terminated PU/epoxy blend (magnification $\times 35$).



(\leftarrow : Crack propagated from right to left)

Figure 9 Optical micrograph of the appearance of clear lateral construction around the crack tip of 10 phr glycidyl-terminated PU/epoxy blend.

terminated from a knowledge of the curing rate of the two prepolymers. Figure 11 shows the DSC curve of the curing reaction of glycidyl-terminated PU and epoxy resins with curing agent separately. From Figure 11, it can be seen that the curing rates of the two prepolymers are different, epoxy resins are more reactive than the glycidyl-terminated PU toward the polyoxypropyleneamine (D-230) curing agent. The curing agent will react with both prepolymers, but preferentially with epoxy resins. Due to the differences in curing rate between glycidyl-terminated PU

and epoxy resins, microphase separation may take place. Microphase separation can be improved by the "prereacted" technique. Because of the slow curing rate between glycidyl-terminated PU and the curing agent, the glycidyl-terminated PU prereacted with the curing agent and then dispersed in epoxy resin homogeneously. Consequently, a homogeneous structure was found in the cured resin.

Various experimental methods have been studied for the assessment of the degree of phase separation, such as mechanical, dynamic mechanical, dielectric measurement, light transmission, optical microscopy, and DSC.^{15,16} The effect of preparative procedures on mechanical properties is shown in Table VI. It was found that the synthesized glycidyl-terminated PU, prereacted with curing agents, can slightly increase mechanical properties over that from the "simultaneous" process. This improvement in mechanical properties may be due to the increase in the degree of compatibility. The extent of mixing of the glycidyl-terminated PU and epoxy phases can be exhibited, at least qualitatively, by the dynamic mechanical and optical behavior of the material. The glass transition temperature (T_g) was derived from the peak temperature of the $\tan\delta$ curve. When two polymers are mixed, the dynamic mechanical behavior will show two distinct transitions, indicating incompatibility between the two polymers. As the compatibility increases, these two T_g s shift toward each other and the damping curve ($\tan\delta$) becomes broader. The T_g s and the optical clarity of the glycidyl-terminated PU/epoxy are shown in Figures 12

Table VI Effect of Different Preparation Procedures on Mechanical Properties

Property	Glycidyl-Terminated PU Content (phr)				
	5	10	15	20	25
Tensile strength (MPa)					
Simultaneous	59.5 ± 0.3	56.6 ± 1.7	52.7 ± 0.2	48.4 ± 0.7	46.1 ± 0.3
Prereaction	63.5 ± 1.2	60.7 ± 1.5	56.8 ± 0.8	52.7 ± 0.5	48.2 ± 0.5
Tensile modulus (MPa)					
Simultaneous	2212 ± 23	2065 ± 36	2015 ± 127	1811 ± 118	1599 ± 132
Prereaction	2302 ± 75	2241 ± 112	1998 ± 87	1922 ± 78	1801 ± 125
Flexural strength (MPa)					
Simultaneous	99.8 ± 1.0	94.0 ± 1.5	88.2 ± 1.3	82.1 ± 1.6	73.9 ± 2.0
Prereaction	107.2 ± 2.3	102.1 ± 1.7	95.1 ± 0.9	85.6 ± 1.2	80.2 ± 1.3
Flexural modulus (MPa)					
Simultaneous	2468 ± 14	2265 ± 55	2196 ± 60	1996 ± 40	1893 ± 23
Prereaction	2585 ± 65	2434 ± 43	2256 ± 75	2014 ± 23	1905 ± 16

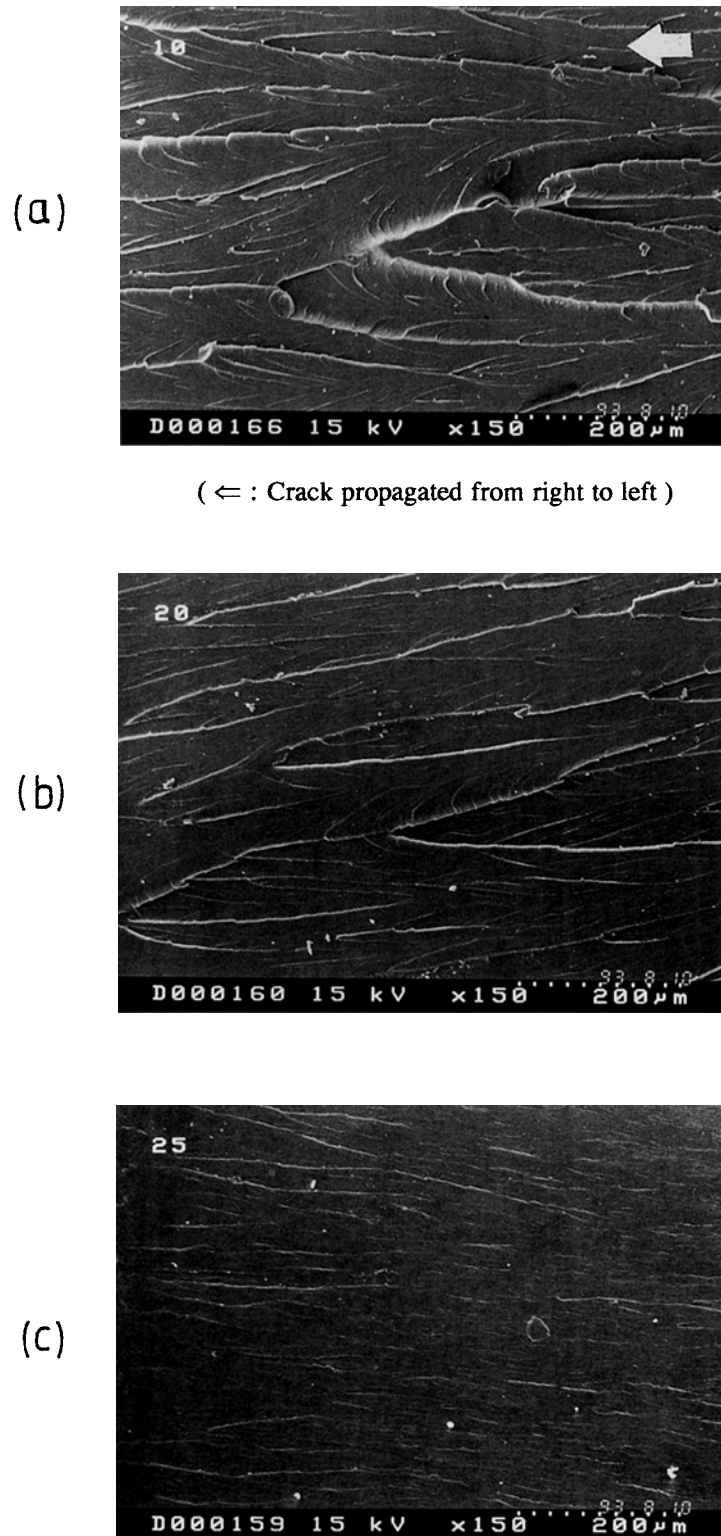


Figure 10 Scanning electron micrograph of the fracture surface of fracture energy test specimen of glycidyl-terminated PU/epoxy with various glycidyl-terminated PU contents. (a) 10 phr glycidyl-terminated PU/epoxy blend, (b) 20 phr glycidyl-terminated PU/epoxy blend, and (c) 25 phr glycidyl-terminated PU/epoxy blend (magnification $\times 150$).

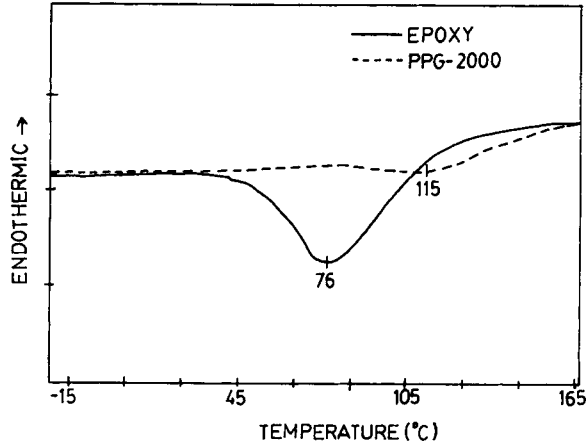


Figure 11 DSC curve of glycidyl-terminated PU and epoxy resin with curing agent separately.

and 13, respectively. From Figures 12 and 13, it was found that the opaque plate, as well as two T_g s, were observed for the “simultaneous” sample. For the “prereacted” sample, there was a translucent appearance, as well as an inward shift of the two glass transition temperatures, indicating the improvement of microphase separation in this case.

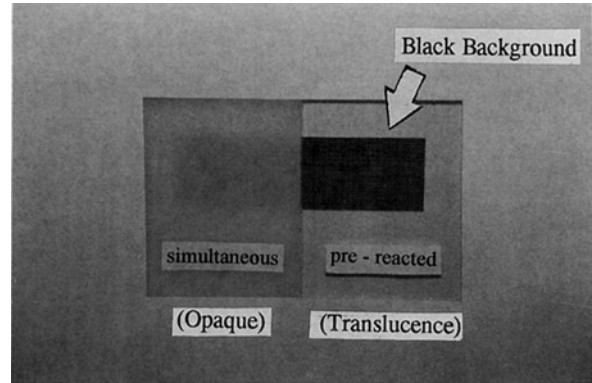


Figure 12 Effect of different preparation procedures on optical clarity of glycidyl-terminated PU/epoxy.

CONCLUSIONS

Significant improvements in the impact properties, fracture energy, and adhesion properties at cryogenic temperature of epoxy resins can be achieved when glycidyl-terminated polyurethanes are mixed with the epoxy resin. It was found that the impact strength and the adhesion strength of modified epoxy resins were greater than those of the pure epoxy resins, showing the ductile fracture without

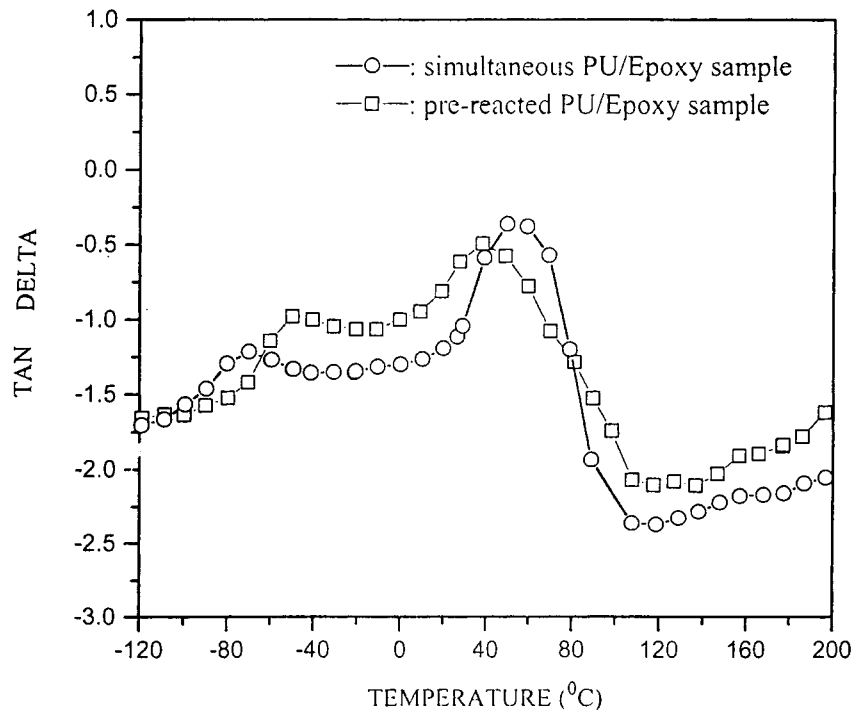


Figure 13 Temperature dependence of $\tan\delta$ for glycidyl-terminated PU/epoxy.

an appreciable sacrifice of flexural and tensile strength.

Because of the difference in the curing rate between the glycidyl-terminated PU and epoxy resin, the system shows phase separation. The phase separation can be improved by prereacting glycidyl-terminated PU with the curing agent. This phenomenon was observed by dynamic mechanical analysis, scanning electron microscopy, and optical microscopy. From the dynamical mechanical analysis, it was found that the two glass transition temperatures shifted inwardly. The effect of preparation procedures on the mechanical properties and morphology of the system is explicit.

This research was financially supported by the National Science Council, Republic of China, under the Contract No. NSC82-0416-E007-155.

REFERENCES

1. C. A. May, in: *Epoxy Resins, Chemistry and Technology*, Marcel Dekker, New York, 1988, p. 551.
2. J. D. LeMay and F. N. Kelley, in: *Structure and Ultimate Properties of Epoxy Resins, Advances in Polymer Science*, K. Dusek, Ed., Springer-Verlag, New York, 1986, vol. 78, p. 115.
3. H. Ng and I. Manas-Zloczower, *Polym. Eng. Sci.*, **33**(4), 211 (1993).
4. R. Drakf and A. Siebert, *SAMPE Quarterly*, **July**, 11 (1975).
5. C. K. Riew and J. K. Gillham, in: *Rubber-Modified Termoset Resins*, Adv. Chem. Series #208, American Chemical Society, Washington, DC, 1984.
6. H. S.-Y. Hsieh, *Polym. Eng. Sci.*, **30**(9), 493 (1990).
7. J. A. Bishopp, *Int. J. Adhesion and Adhesives*, **12**(3), 178 (1992).
8. K. H. Miska, *Mater. Engin.*, **5**, 45 (1978).
9. J. L. Han, S. M. Tseng, J. H. Mai, and K. H. Hsieh, *Die Ang. Markro, Chem.*, **182**, 193 (1990).
10. G. Oertel, in: *Polyurethane Handbook*, Hanser, Munich, 1985, p. 522.
11. R. T. Agger, *Int. J. Adhesion and Adhesives*, **4**(4), 151 (1984).
12. Z. W. Wicks, *Prog., Org., Coating*, **3**, 73 (1975).
13. R. L. Jacobs and J. W. Long, *J. Elast. Plast.*, **11**, 15 (1979).
14. C. C. Ma, D. S. Chen, H. C. Hsia, W. N. Wang, and S. R. Li, *J. Appl. Polym. Sci.*, to appear.
15. T. T. Wang and H. M. Zupko, *J. Appl. Polym. Sci.*, **26**, 2391 (1981).
16. Z. S. Petrovic, *J. Polym. Sci. Part B Polym. Phys.*, **27**, 545 (1989).
17. A. Wilford, T. C. P. Lee, and T. J. Kemp, *Int. J. Adhesion and Adhesives*, **12**(3), 171 (1992).
18. A. H. Landrock, in: *Adhesives Technology Handbook*, Noyes, New Jersey, 1985, p. 64.
19. R. T. Ting and R. L. Cottingham, *J. Appl. Polym. Sci.*, **25**, 1815 (1980).
20. C. B. Lee and F. C. Chang, *Polym. Eng. Sci.*, **32**(12), 792 (1992).
21. ASTM E813-89, *Standard Test Method for J_{Ic} , A Measure of Fracture Toughness*.
22. S. S. Labana, in: *Crosslinking, Encyclopedia of Polymer Science and Engineering*, H. F. Mark, Eds., Wiley, New York, 1985, vol. 4, p. 350.
23. S. R. Sandler and F. R. Berg, *J. Appl. Polym. Sci.*, **9**, 3909 (1965).
24. L. M. Roseland, *J. Macromol Sci-Phys.*, **B**(4), 639 (1967).
25. R. B. Gosnell and H. H. Levine, *J. Macromol Sci-Chem.*, **A3**(7), 1381 (1969).
26. J. F. Huang, J. A. Manson, R. W. Hertzberg, G. A. Miller, and L. H. Sperling, *Polym. Eng. Sci.*, **29**(20), 1466 (1989).
27. D. Broek, *Elementary Engineering Fracture Mechanics*, 4th Ed., Martinus Nijhoff, Boston, 1986, p. 30.
28. D. Broek, *Elementary Engineering Fracture Mechanics*, 4th Ed., Martinus Nijhoff, Boston, 1986, p. 140.
29. E. Pink and J. D. Campbell, *Mater. Sci. Eng.*, **15**, 187 (1974).
30. M. J. Zhang, F. X. Zhi, and X. R. Sn, *Polym. Eng. Sci.*, **29**, 1142 (1989).
31. R. A. W. Fraser and I. M. Ward, *J. Mater. Sci.*, **12**, 459 (1977).
32. A. F. Yee, *J. Mater. Sci.*, **12**, 757 (1977).
33. F. C. Chang, J. S. Wu, and L. H. Chu, *J. Appl. Polym. Sci.*, **44**, 494 (1992).
34. F. C. Chang and L. H. Chu, *J. Appl. Polym. Sci.*, **44**, 1618 (1992).

Received September 22, 1993

Accepted November 23, 1993