Studies on Isotactic Poly(phenyl glycidyl ether)-Modified Epoxy Resins. II. Toughening of Epoxy Resins

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ABSTRACT: A semicrystalline polymer, isotactic poly(phenyl glycidyl ether) (i-PPGE) was used as a modifier for epoxy resin; 1,8-Diamino-p-methane (MNDA) and 4,4′-Diamino diphenyl sulfone (DDS) were used as curing agents. In the MNDA-cured resins, the dispersed phase were spherical particles with diameters in the range of 0.5–1.0 μm when the resin was blended with 5 phr i-PPGE. In the DDS-cured resins, the particle size distribution of the dispersed phase was much wider. The difference was traced back to the reactivity of the curing agent and the different regimes used for curing. Through dynamic mechanical analysis, it was found that in the MNDA-cured systems, i-PPGE had a lower crystallinity than in the DDS-cured system. In spite of the remarkable difference in the morphology and microstructure of the modified resins cured with these two curing agents, the toughening effects of i-PPGE were similar for these resins. The critical stress intensity factor (K_{IC}) was increased by 54% and 53%, respectively, for the resins cured by DDS and by MNDA, blending with 5 phr of the toughner. i-PPGE was comparable with the classical toughners carboxyl-terminated butadiene-acrylonitrile copolymers in effectiveness of toughening the epoxy resin. An advantage of i-PPGE was that the modulus and the glass-transition temperature of the resin were less affected. However, this modifier caused the flexural strength to decrease somewhat. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1223–1232, 2002; DOI 10.1002/app.10445

Key Words: epoxy resin; poly(phenyl glycidyl ether); toughness

INTRODUCTION

Multiphase systems of epoxy resins have been developed for improving the toughness of the resins. Classical toughening agents are reactive rubbers such as carboxyl-terminated butadiene-acrylonitrile copolymers (CTBNs) and amino-terminated butadiene-acrylonitrile copolymers (AT-BNs).[1–3] Preformed rubber particles in the form of reactive microgels and core-shell particles have been developed.[4,5] Now rubber-toughened epoxy systems are used extensively in structural adhesive systems.

Rubber-toughened epoxy systems have greatly improved toughness and significantly reduced modulus. Reduction of modulus is desirable for structural adhesives, as a lower modulus favors even stress distribution along the bond line. However, for the matrix of composites, lowering of the modulus is unfavorable.
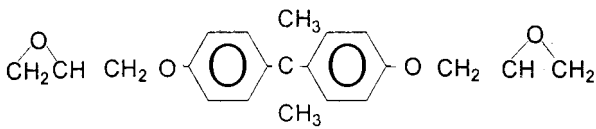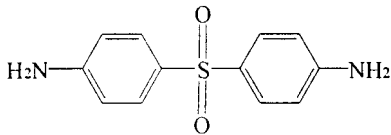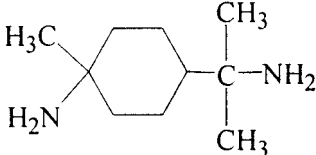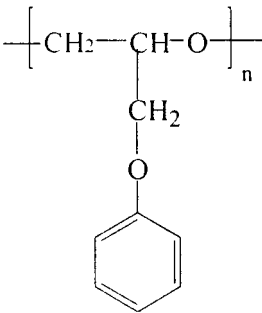
To improve the toughness without sacrificing modulus and strength, high-performance thermoplastics such as polyethersulphone, polysulphone, polyetherimide, and polyphenylene oxide were blended with epoxy resins.[6–9]

Semicrystalline polymers are an interesting option for the toughening the epoxy resin, as phase transformation of the crystalline polymer might provide an additional mechanism for the

Table I   Materials Used in This Work

Material	Formulae	Description
Epoxy resin $CH_2CH\ CH_2\ O$		Epon 828 Epoxy value 5.3 meq/g
4,4′-Diamino diphenyl sulphone		Chemical reagent
1,8-Diamino-p-methane		Chemical reagent
Isotactic poly(phenyl glycidyl ether)		$[\eta]$ 0.65 dL/g (TCE, 30°C) Isotacticity 82%

toughening,[10–12] and study has been devoted to poly(butylene terephthalate) (PBT).[13–16] According to Nichols and Rorbertson,[14] the toughening effect was highly dependent on the morphology of the, crystallite dispersed in the epoxy resin, and a very high level of toughness was achieved when the polymer formed a structureless gel.[14] Nylon 6 and polyvinylidene difluoride were reported to toughen epoxy resin as effectively as the CTBN rubber.[13] Poly(oxymethylene) POM was not very effective in toughening epoxy resin when applied alone.[17]

As the mechanism for the toughening of thermosetting resins is very complicated, the development of good toughened systems is usually based on careful experimental studies. Our-work characterizes a new system, where an i-PPGE, which can be prepared by stereoregular polymerization under the effect of a coordination catalyst,[18–22] is used as a modifier of the epoxy resin. The monomer phenyl glycidyl ether can be looked at structurally as a half of diglycidyl ether of bisphenol-A (DGEBA). Therefore, i-PPGE may have good compatibility with the epoxy resin. In Zhang et al.[23]

physical gels of i-PPGE in the epoxy resin have been studied. It is interesting to note the toughening effect of this semicrystalline polymer. This article deals with the morphology development in the i-PPGE/epoxy resin system and the mechanical properties of the cured resins.

EXPERIMENTAL

Materials

Materials used in this study are listed in Table I. The epoxy resin EPON 828 was DGEBA, obtained from Shell Company (The Netherlands). 4,4′-Diamino diphenyl sulfone (DDS) was a chemical reagent from Beijing Chemical Factory (China). It was ground to pass through a sieve of mesh No. 200, and dried in vacuum at 100°C for 2 h before use. 1,8-Diamino-p-methane (MNDA) was provided by Aldrich Chemical Company (USA) and was used without further purification.

i-PPGE was prepared according to the process described in Zhana et al.[23] The polymer was at-

tracted with acetone to remove the atactic fraction. The isotactic fraction was used in this study. The diad isotacticity was 82%, determined by ^{13}C-NMR analysis,[24] intrinsic viscosity in tetrachloroethane at 30°C was 0.65 dL/g.

CTBN of molecular weight 3000 and acrylonitrile content of 25% was from Lanzhou Research Institute of Chemical Industry (China). It was used for comparison.

Preparation of i-PPGE-Modified Epoxy Resin

Two procedures were used for the preparation of specimens. When DDS was used as curing agent, i-PPGE was dissolved in the epoxy resin at 200°C. The solution was cooled to approximately 180°C, and the curing agent in stoichiometric ratio was added. After vigorous stirring for a few minutes, the curing agent was dissolved completely. A vacuum was applied to remove the trapped gas, and the resin then was cast into a preheated mold and cured at 125°C for 2 h and then at 200°C for 2 h.

When MNDA was used as the curing agent, i-PPGE was dissolved in the epoxy resin at 200°C. The solution was cooled to approximately 80°C, and the curing agent was added in stoichiometric ratio. After dissolution of the curing agent, the resin was deaired in vacuum and cast into a mold. Curing was effected at 80°C for 2 h and at 160°C for 2 h.

Characterization

Differential scanning calorimetry (DSC) was conducted on a TA 2100 Modulated differential scanning calorimeter (TA Instruments, Inc., USA) at a heating rate of 10°C/min under a nitrogen atmosphere.

The dynamic mechanical analysis (DMA) was performed using a Rheometric Scientific DMTA IV with the specimen dimensions of $30 \times 6 \times 2$ mm^3. The measurements were carried out at a frequency of 1 Hz under a nitrogen atmosphere. The temperature was increased from -150 to 250°C at a heating rate of 5°C/min. The peak temperature of the tan δ was taken as the glass-transition temperature.

For morphology studies, the fracture surface of the specimens was examined under a Hitachi S-530 scanning electron microscope (SEM) (Japan).

A three-point bending test was performed at room temperature according to the standard GB 1042 to determine the flexural properties of the cured resins. The specimens were $4 \times 6 \times 55$-mm^3 rectangular bars. The measurement was conducted on an Instron 1122 mechanical tester (USA). The support span was 48 mm, and the crosshead speed was 10 mm/min for the flexural strength determination and 2 mm/min for the flexural modulus determination. The average value was taken from fine specimens.

The fracture toughness at room temperature was measured using single-edge notch (SEN) specimens according to ASTM E399. The specimens were $10 \times 12 \times 60$-mm^3 rectangular bars. There was a notch of 0.3 mm in thickness and 4 mm in depth in the middle of the specimen, which was made with a saw. A fine precrack was made in the notch by tapping a razor blade chilled with liquid nitrogen. The measurement was conducted on an Instron 1122 Mechanical Tester. The support span was 48 mm, and the crosshead speed was 2 mm/min.

The critical stress intensity factor, K_{IC}, was obtained using the formula

$$K_{IC} = (6F_C Y a^{0.5})/\sqrt{10} BW, \tag{1}$$

where F_c was the load at failure, B was the thickness of the specimen, W was the depth of the specimen, and a was the crack length. The specimen shape factor Y was a function of the dimensionless parameter a/W.

$$Y = \frac{1.99 - \{aW(1 - aW)[2.15 - 3.93aW + 2.7(aW)^2]\}}{(1 + 2aW)(1 - aW)^{1.5}}. \tag{2}$$

The fracture toughness was obtained,

$$G_{IC} = 880 K_{IC^2}/E_b, \tag{3}$$

where E_b was the flexural modulus of the specimen.

RESULTS AND DISCUSSION

Morphology Development in the i-PPGE/Epoxy Resin Systems

i-PPGE is a semicrystalline polymer with a melting temperature in the range of 180–190°C. It was dissolved in the epoxy resin at 200°C to form a clear solution. When the solution was cooled to directly room temperature, the crystallites of i-
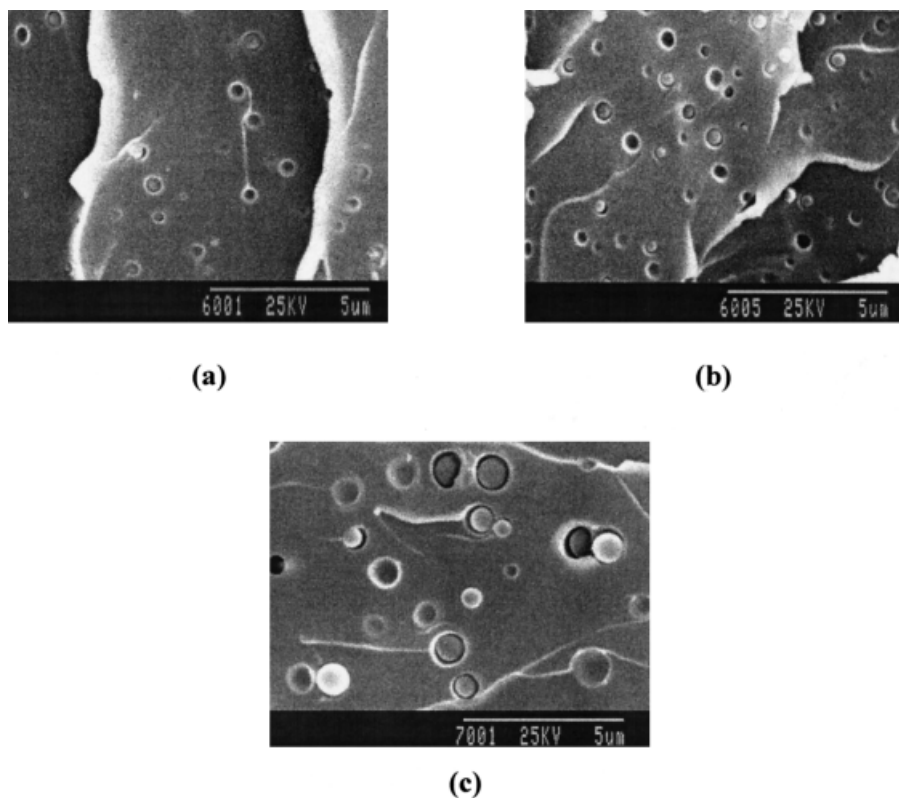
Figure 1   Scanning electron microscope photos of the 1,8-Diamino-p-methane-cured-epoxy resins modified with (a) 1 phr isotactic poly(phenyl glycidyl ether) (i-PPGE) (10,000×), (b) 3 phr i-PPGE (10,000×), (c) 5 phr a-PPGE (10,000×).

PPGE were submicron size. They formed a network, and the system became a gel.[23] The gels of i-PPGE in epoxy resin were stable at temperatures below 120°C. No changes were found after staying for long times. However, when a curing agent was introduced to the resin, the turbidity increased gradually as the curing went on. Obviously, the phase of i-PPGE was changing on curing.

To illustrate the behavior of morphology development, two curing agents of different reactivity were used. MNDA was an aliphatic amine. As the
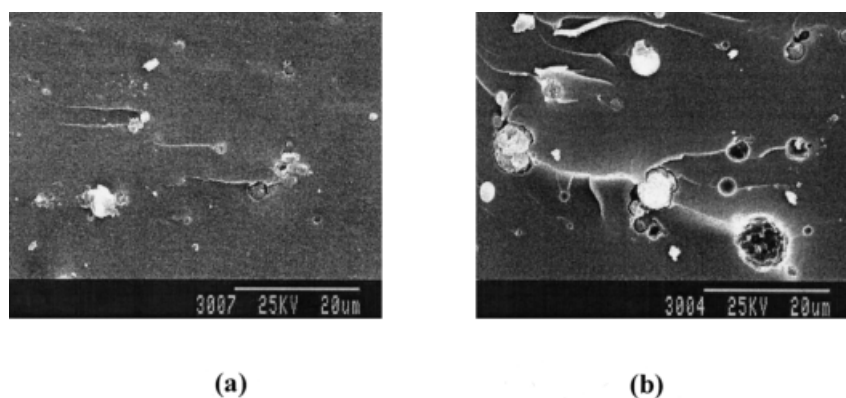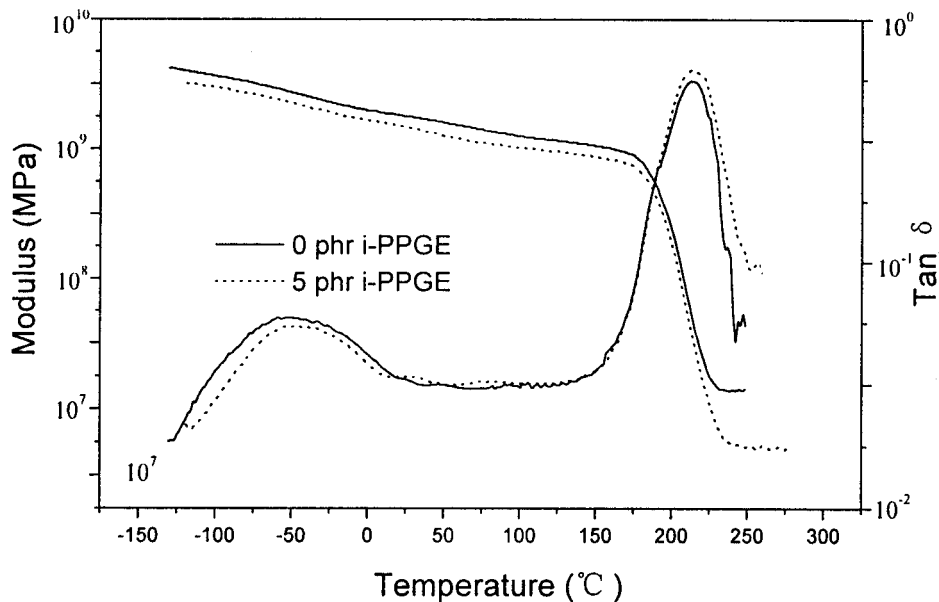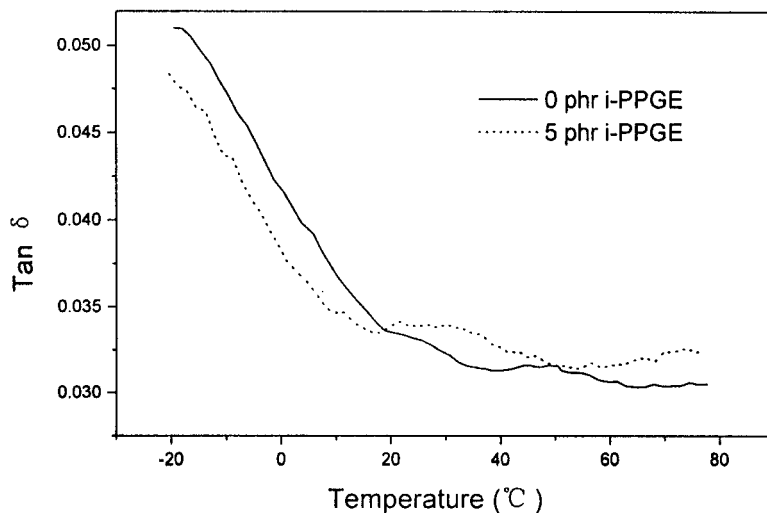

Figure 2   Scanning electron microscope photos of the 4,4′-Diamino diphenyl sulfone-cured epoxy resins modified with (a) 3 phr isotactic poly (phenyl glycidyl ether) (i-PPGE) (2000 ×) and (b) 5 phr i-PPGE (2000 ×).
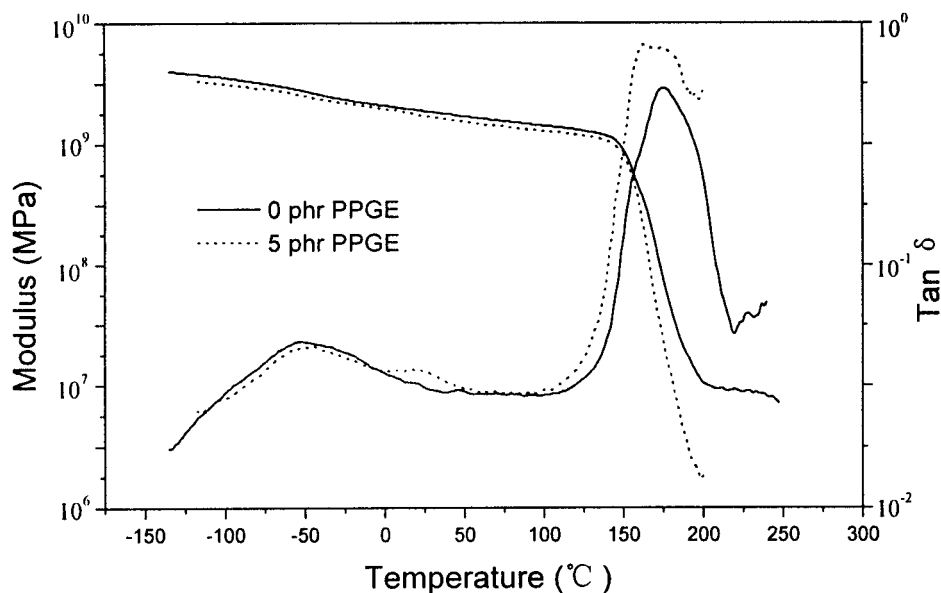
(a)

(b)

Figure 3 Dynamic mechanical spectra of the 4,4′-Diamino diphenyl sulfone-cured epoxy resins containing 0 phr and 5 phr isotactic poly(phenyl glycidyl ether).

solution of i-PPGE was cooled to 80°C, the curing agent was added. The postcuring was carried at 160°C, a temperature well below the melting temperature of i-PPGE.

The morphology of the i-PPGE/epoxy resin cured with MNDA is shown in Figure 1. It can be seen

that the dispersed phase in the SEM pictures are spherical particles. The size increased with the concentration of i-PPGE. For the resin with 5 phr of i-PPGE, the particle size ranged from 0.5 to 1 μm.

DDS was an aromatic amine. Precuring was carried out at 125°C, which was favorable to the

(a)
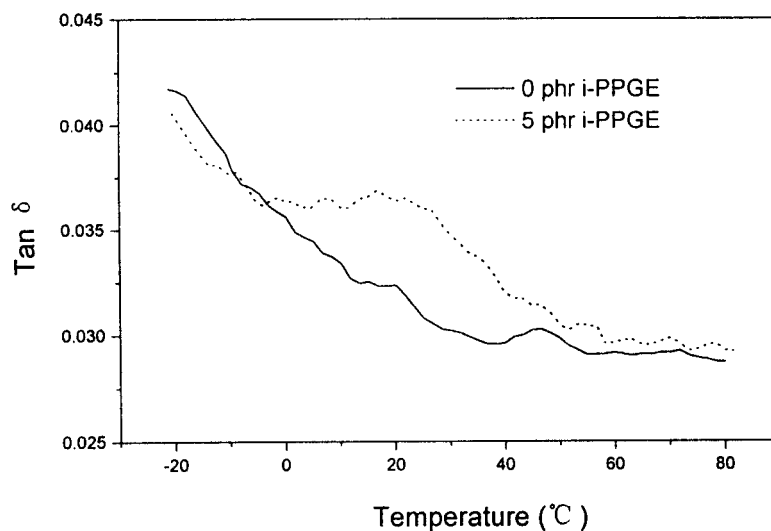
(b)

Figure 4 Dynamic mechanical spectra of the 1, 8-Diamino-p-methane-cured epoxy resins containing 0 and 5 phr isotactic poly(phenyl glycidyl ether).

growth of the i-PPGE crystallites. Postcuring was carried out at 200°C, a temperature above the melting temperature.

The morphology of DDS-cured resins is shown in Figure 2. Compared with the resin cured with MNDA, remarkable differences can be seen.

Many particles of 7–8 μm in diameter, along with many small particles of a diameter less than 1 μm, can be seen in the resin with 5 phr of i-PPGE. Some particles have an irregular form. It seems that the large particles were formed through agglomeration of small particles.

Table II Properties of Epoxy Resins Cured with 4,4′ = Diamino Diphenyl Sulfone

Additive/ concentration (phr)	Flexural Properties		Fracture Properties	Glass-transition temperature	
	Strength (MPa)	Modulus (GPa)	K_{1c} (MPa m^{1,2})	DSC (°C)	DMA (°C)
i-PPGE/0	141 ± 4	2.36 ± 0.02	0.625 ± 0.04	199	212
i-PPGE/1	145 ± 9	2.39 ± 0.05	0.763 ± 0.06	200	—
i-PPGE/3	123 ± 17	2.31 ± 0.04	0.816 ± 0.09	194	—
i-PPGE/5	116 ± 7	2.34 ± 0.03	0.965 ± 0.11	196	213
i-PPGE/5	116 ± 3	2.28 ± 0.08	1.05 ± 0.22	195	216
CTBN/5	141 ± 17	2.06 ± 0.08	0.898 ± 0.10	193	—

i = PPGE = isotactic poly (phenyl glycidyl ether); CTBN = carboxyl-terminated butadine-acrylonitrile copolymers; DSC = differential scanning calorimetry; DMA = dynamic mechanical analysis; K_{IC} = critical stress intensity factor

The differences in the morphology of i-PPGE-modified epoxy resins cured with MNDA and DDS can be traced back to the cure behavior of the resin systems. In the system with MNDA as curing agent, the precure was conducted at 80°C. The time interval for particle growth of the second phase was short, as gelation and vitrification were very fast; after that, the morphology was frozen. The reactivity of DDS was much lower. In the system with DDS as curing agent, the precure was conducted at 125°C. In this case, the viscosity of the system was low, and the time interval for particle growth was long. Consequently, many large particles were formed.

It can be seen in Figure 2 that the large particles in the DDS-cured systems have a rough and irregular fracture surface. This feature may be attributed to the perfectness of crystallization. As the curing temperature was above the melting temperature of i-PPGE, recrystallization took place after the curing. This process may result in more perfect crystalline particles.

Dynamic Mechanical Analysis

The mechanical damping is very sensitive to the microstructures of the material. To get more information about the two-phase materials of i-PPGE-modified epoxy resins, dynamic mechanical analysis was carried out. Mechanical spectra of i-PPGE-modified epoxy resins are given in Figures 3 and 4.
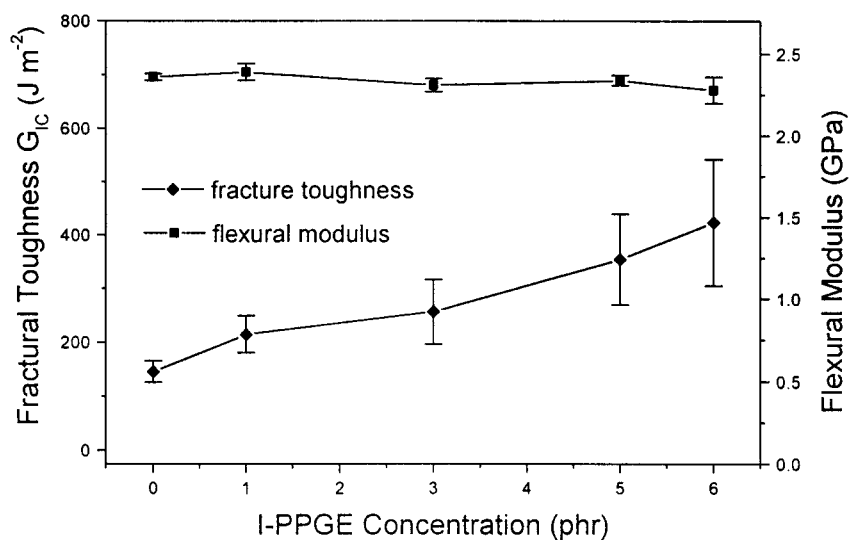

Figure 5 The fracture toughness and flexural modulus vs. concentration of isotactic poly(phenyl glycidyl ether) for epoxy resins cured with 4,4′-diamino diphenyl sulfone.

Table III   Properties of Epoxy Resins Cured with 1: = Diamino p = methane

i-PPGE Concentration (phr)	Flexural Properties		Fracture Properties	Glass Transition Temperature	
	Strength (MPa)	Modulus (GPa)	K_{IC} (MPa.m$^{-1/2}$)	DSC (°C)	DMA (°C)
0	140 ± 10	2.39 ± 0.02	0.535 ± 0.06	157	175
1	137 ± 4	2.28 ± 0.05	0.621 ± 0.07	159	—
3	105 ± 19	2.43 ± 0.09	0.804 ± 0.01	156	170, 176
5	106 ± 27	2.36 ± 0.09	0.816 ± 0.06	154	167,175

i = PPGE = isotactic poly(phenyl glycidyl ether); K_{IC} = critical stress intensity factor; DSC = differential scanning calorimetry; DMA = dynamic mechanical analysis.

It can be seen in Figure 3(a) that the glass-transition temperature of the resin cured with DDS was practically unaffected by introduction of i-PPGE. It means that the phase separation was complete. The glass-transition temperature for the amorphous phase of the neat i-PPGE was 32°C, determined by DMA. For the modified resin cured with DDS, a damping peak is visible in this region (Fig. 3b). The damping peak was very low, which indicated that i-PPGE in the modified epoxy resin had a high degree of crystallinity.

For the MNDA-cured resin, the damping peak for the glass transition of the resin changed significantly. As 5 phr of i-PPGE was incorporated, a damping peak appeared at 167°C in addition to the peak at 175°C for the neat resin (Fig. 4[a]). This new peak may be from the interfacial region of the two phases, where the glass-transition temperature of the resin was depressed by a fraction of i-PPGE dissolved in the resin.

The damping peak for i-PPGE in the MNDA-cured resin was shifted to lower temperatures (Fig. 4[b]). The peak was higher compared with that in the DDS-cured resin of the same modifier content. A higher damping peak means a greater concentration of the amorphous phase. Therefore, the crystallinity of i-PPGE in the MNDA-cured resin was lower.

The reason for a lower crystallinity of i-PPGE in the MNDA-cured resin was twofold. First, a fraction of i-PPGE was dissolved in the resin at the interfacial region, as stated above, that did not crystallize. Moreover, the agglomerates of crystallites in the dispersed phase did not have a melting and recrystallization process to create a more perfect crystallization, as the temperature
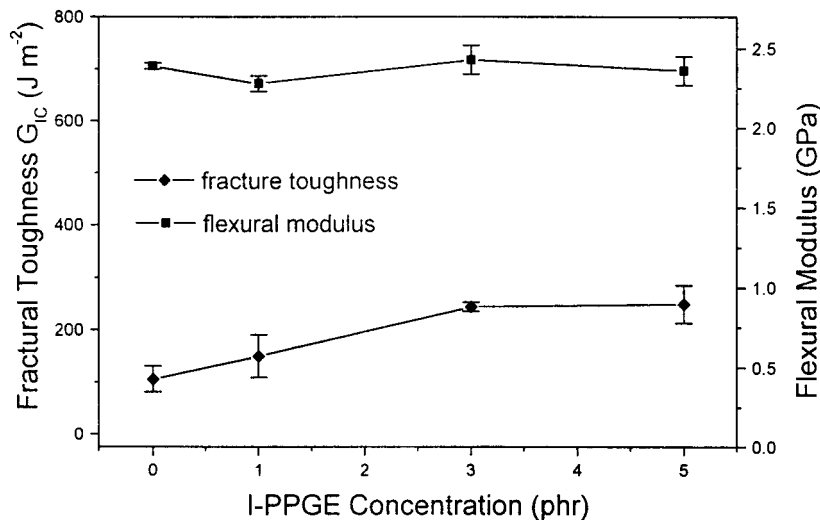

Figure 6   The fracture toughness and flexural modulus versus concentration of isotactic poly(phenyl glycidyl ether) for epoxy resins cured with 1,8-diamino-p-methane.

for curing was well below the melting temperature.

Mechanical Properties

The mechanical properties and the glass-transition temperature of the DDS-cured resins are listed in Table II. It should be stated that only specimens with a low i-PPGE concentration (<6 phr) were tested. Cured systems with higher i-PPGE concentrations were hard to process because of the physical gelation, which made casting and removing trapped gas impossible.

It can be seen that the critical stress intensity factor K_{IC} increased consistently with the content of i-PPGE. For the resin containing 5 phr i-PPGE, an increase of K_{IC} by 54% was measured. However, the modifier caused a loss of the flexural strength by 18%.

A plot of fracture toughness (G_{IC}) and the flexural modulus versus the concentration of i-PPGE is shown in Figure 5. It can be seen that the fracture toughness of the resin was improved without significant influence on the modulus.

The toughness improvement of i-PPGE was comparable with that of the classical toughner CTBN. The toughening mechanism in the rubber-modified epoxy resin has been examined in many studies.[25–27] The fracture improvement usually was achieved at the cost of modulus, as the modulus of the rubber phase was low and a fraction of the rubber was dissolved in the cured resin matrix. A significant decrease in the glass-transition temperature T_g was caused by CTBN as well.

Similar toughness improvements were achieved for the epoxy resins cured with MNDA and those cured with DDS, in spite of the remarkable difference in the morphology and microstructure. The properties of the MNDA-cured resins are listed in Table III. A plot of fracture toughness and the flexural modulus versus i-PPGE concentration is given in Figure 6. It can be seen that K_{IC} improved consistently with the content of the modifier. An increase of 53% was achieved by the incorporation of 5 phr i-PPGE, whereas the flexural modulus was not affected significantly. Again, significant losses in the flexural strength were found with the incorporation of the modifier.

CONCLUSIONS

In the i-PPGE-modified epoxy resins, the morphology was dependent on the concentration of the modifier and on the kind of curing agent used. In the MNDA-cured resins containing 5 phr of the modifier, the dispersed phase was spherical particles of diameter in the range of 0.5 to 1 μm. On condition that DDS was used as the curing agent, the particle size distribution was much wider; many particles 7–8 μm in diameter, along with many small particles with a diameter of approximately 0.5 μm were there. It was found by DMA analysis that in the DDS-cured resin the phase separation was complete. In the MNDA-cured system, a fraction of the modifier was in the interfacial region, and the crystallinity of i-PPGE was lower. In spite of the remarkable difference in the morphology and microstructure in the resins cured with these two curing agents, the toughening effects of i-PPGE were similar for these resin systems. The critical stress intensity factor K_{IC} increased consistently with the content of i-PPGE. i-PPGE was comparable with the classical toughner CTBN in effectiveness of toughening the epoxy resin. An advantage of i-PPGE was that the modulus and the glass-transition temperature of the resin were less affected. However, the flexural strength was somewhat decreased by this modifier.

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