

Cure Behavior, Morphology, and Mechanical Properties of the Melt Blends of Epoxy with Polyphenylene Oxide

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ABSTRACT: Cure behavior, miscibility, and phase separation have been studied in blends of polyphenylene oxide (PPO) with diglycidyl ether of bisphenol A (DGEBA) resin and cyanate ester hardener. An autocatalytic mechanism was observed for the epoxy/PPO blends and the neat epoxy. It was also found that the epoxy/PPO blends react faster than the neat epoxy. During cure, the epoxy resin is polymerized, and the reaction-induced phase separation is accompanied by phase inversion upon the concentration of PPO greater than 50 phr. The dynamic mechanical measurements indicate that the two-phase character and partial mixing existed in all the mixtures. However, the two-phase particulate morphology was not uniform especially at a low PPO content. In order to improve the uniformity and miscibility, triallylisocyanurate (TAIC) was evaluated as an in situ compatibilizer for epoxy/PPO blends. TAIC is miscible in epoxy, and the PPO chains are bound to TAIC network. SEM observations show that adding TAIC improves the miscibility and solvent resistance of the epoxy/PPO blends. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 26–34, 2000

Key words: epoxy/PPO blends; cure behavior; miscibility; triallylisocyanurate

The use of rubber modification of epoxy resins to improve the fracture toughness has been known for a considerable time.^{1–4} However, the rubber modification of epoxies becomes ineffective as the cross-link density of the epoxy matrix increases due to the inability of the rubber particles to deform by shear yielding or cavitation. Furthermore, the improvements in fracture toughness of these rubber-modified epoxy systems usually result in a significant decrease in modulus,^{2,3} yield strength, and the glass transition temperature (T_g) of the cured epoxy resins. Fortunately, a new toughening technology can enhance fracture toughness without sacrificing the mechanical properties of thermosetting resin system. This new technology uses high modulus, high glass

transition temperature thermoplastics to toughen thermosetting polymers.^{5–11}

A classical example is polyphenylene oxide (PPO),^{9,10} an amorphous thermoplastic with a low dielectric constant, a low dissipation factor, and high glass transition temperature. PPO has other excellent properties, such as low water absorption, solvent resistance, considerable impact strength, and excellent peel strength to copper foil. But PPO resin has no ability in miscibility with epoxy resin because PPO has no polarity in nature. This paper concerns the toughening of an epoxy resin using a thermoplastic PPO. The cure kinetic analysis of epoxy/PPO blend was examined by differential scanning calorimetry (DSC). Phase morphology of cured material was investigated by dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). Furthermore, we shall describe the use of a reactive monomer triallylisocyanurate (TAIC) to stabilize the particulate morphology of these two phase materials.

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This is a new method that a reactive monomer has been added to improve the miscibility of thermoplastic modified epoxies.

EXPERIMENTAL

Materials

The epoxy resin was a commercial diglycidyl-type resin (Epon 828, Shell) and the curing agent was multifunctional cyanate ester (PT-30, Lonza). The thermoplastic polymer used was poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, GE) with an intrinsic viscosity of 0.4 dL g^{-1} measured in chloroform at 25°C . In this investigation, the reactive monomer, triallylisocyanurate (TAIC, ACROS), was used as compatibilizer for epoxy/PPO blends.

Blend Preparation

Series 1: The Effect of PPO Concentration.

Solutions of PPO in epoxy resin, with a PPO content ≤ 50 phr, were prepared by dissolving PPO in the epoxy resin by using a mechanical stirrer at temperature $\leq 170^\circ\text{C}$ (where phr represents the number of parts of PPO per hundred parts of the epoxy resin). The solutions were cured by using cyanate ester. The curing agent (20 phr) was added to the homogeneous solution and after mixing for 2 min, the compound was poured into a preheated mold and cured under ambient conditions for 4 h at 180°C , followed by 4 h at 220°C .

Series 2: The Use of TAIC Monomer.

Three TAIC concentrations, 5, 10, and 20 phr, were examined. The mixing procedure was that epoxy and PPO were dissolved first, and then cyanate ester and TAIC were added. The remainder of the cure conditions was the same as described series 1.

Differential Scanning Calorimetry

The cure reaction of the epoxy/PPO blends was followed by DSC (model 2920, Du Pont). Isothermal cure reaction was conducted at three temperatures (180°C , 190°C , and 200°C). The reaction was considered complete when the isothermal DSC thermogram leveled off to the baseline. The conversions of neat epoxy and epoxy/PPO mixtures were estimated from the relationship $\alpha_1(t) = \Delta H_1(t)/\Delta H_T$, where the value of $\alpha_1(t)$ is determined by measuring the partial heat of reaction

up to time t [$\Delta H_1(t)$] and dividing by the total heat of the reaction (ΔH_T), which can be estimated from a nonisothermal temperature scan ($10^\circ\text{C}/\text{min}$).¹²

Scanning Electron Microscopy

The morphology of the cured resins was determined by using SEM (Hitachi S-2300). The fracture surfaces of samples were mounted and gold-coated by vapour deposition using a vacuum sputter. Some of the fractured samples were etched with dichloromethane at room temperature for 30 min before they were gold-coated and examined by microscopy.

Dynamic Mechanical Analysis

After curing, the blend specimen was allowed to cool slowly to room temperature then was cut into a strip ($10 \times 5 \times 1$ mm) for the dynamic mechanical analysis. The dynamic mechanical behavior was measured by a single cantilever bending test (Du Pont, model 2980). The frequency was fixed at 1 Hz and the scanning rate was $5^\circ\text{C}/\text{min}$ over a wide range of temperature (50 – 250°C).

Mechanical Analysis

The tensile strength and modulus of cured resins were determined according to ASTM 638. Edge-polished specimens (180 mm long, 2 mm thick, and 13 mm wide in the narrow section) were tested on a tensile tester (Instron 1302), at a constant crosshead speed of 1 mm/min at room temperature. The critical strain-energy release rate, G_{IC} , of the cured resins is given by the tapered double cantilever beam (TDCB) method.¹³ The G_{IC} values were calculated by the following equation:

$$G_{IC} = 4P^2m/Ebb'$$

where P is the load required to propagate the crack, E is the tensile modulus, b is the specimen thickness, b' is the side groove thickness, and m is a constant that depends on shape of the specimen and has a value of 3.27 cm^{-1} . Specimens were tested at room temperature on an Instron tester at a crosshead speed of 1 mm/min. Each reported mechanical value is the average of more than 10 successful measurements.

Dielectric Analysis

The dielectric constant of the blend was measured at 1 MHz using an HP-4291A impedance ana-

Table I Dynamic DSC Measurement for Epoxy/PPO Blends with Various PPO Content

PPO Content	T_i (°C) ^a	T_p (°C) ^b	ΔH_T (J/g) ^c
0 phr	235	264	306
10 phr	234	263	303
20 phr	224	250	280
30 phr	218	245	277
50 phr	210	240	274
100 phr	186	221	270

Ramp: 10°C/min from 50°C to 350°C in 40 mL/min N₂.

^a T_i : the onset temperature of heat of reaction.

^b T_p : the maximum peak temperature of heat of reaction.

^c ΔH_T : heat of reaction.

lyzer. The specimens were cut into a strip (20 × 20 × 2 mm) for electrical analysis at room temperature.

RESULTS AND DISCUSSION

Reaction Analysis of Epoxy Blends with PPO

Cure studies of epoxy/PPO blends with 20 phr cyanate ester revealed only one exotherm in the temperature range of 200–300°C. The concentration of PPO was varied from 10 to 50 phr to investigate the effect of concentration on the curing characteristics of epoxy/PPO blends. Curing heat (ΔH_T) of epoxy/PPO blends during a DSC scan at 10°C/min decreased with increase PPO content. Note that calculation of the heats of reaction for the blends was based on the net weight of the epoxy-cyanate ester resin in the blends with the weight of PPO in the epoxy blends being discounted. The decrease of ΔH_T with the increase in PPO should not be taken as a result of the PPO weight in the blend. Rather, this was an indication that the steric and diffusional limitations imposed by the PPO on the formation of the epoxy network during cure accompanied by phase separation may account for the decrease in the total heat of reaction with increasing PPO content. Furthermore, the onset temperature and the maximum peak temperature shifted to low temperature region means that the reaction rate of the epoxy is enhanced by the presence of PPO at the early stage of curing. It may be due to the present of the PPO phenolic end-groups, and cyanate ester tertiary amine resulted in a fast curing rate of the epoxy.^{14–17} The results are shown in Table I.

A dynamic DSC run can be used to determine the appropriate isothermal temperatures. The isothermal temperatures are selected from an interval between 10°C and 20°C below the onset of cure temperature. The maximum heat evolutions of epoxy and blends do not occur in the initial isothermal DSC signal. These results are characteristics of autocatalytic reactions. So the autocatalytic kinetic model [$d\alpha/dt = k\alpha^m(1 - \alpha)^n$] was used and all the plots of $\log(d\alpha/dt)$ against $\log[\alpha^{m/n}(1 - \alpha)]$ show fairly good straight line. As expected from the results reported in Table II, higher isothermal temperature result in higher ultimate conversion, indicating that the reactions would reach diffusion control regions at higher conversions when higher reaction temperatures are used. The incomplete curing reaction obtained in isothermal conditions could be explained in terms of the structural changes produced by polymerization reactions associated with an increase of T_g of the reaction system. Moreover, the decrease in the final conversion in the blend can be ascribed to an increase of the bulk viscosity of the system caused by the presence of PPO. Thus, the T_g of the epoxy phase of the blends measured by DMA showed that the increase of PPO in the blends caused lower T_g for the epoxy phase (Table III).

Table II Isothermal Cure Reaction for Epoxy/PPO Blends with Various PPO Content

PPO Content	t_i (min) ^a	t_p (min) ^b	ΔH_I (J/g) ^c	α (%)
Isothermal, 180°C				
0 phr	17.9	38.7	253	82.7
10 phr	13.2	30.3	242	79.9
30 phr	9.7	24.8	215	77.6
50 phr	6.2	19.2	208	75.9
Isothermal, 190°C				
0 phr	11.4	28.1	296	96.7
10 phr	8.0	24.4	267	88.1
30 phr	6.4	17.1	218	78.7
50 phr	4.5	14.5	212	77.3
Isothermal, 200°C				
0 phr	7.1	19.4	304	99.3
10 phr	5.8	19.7	292	96.4
30 phr	3.4	12.3	220	79.4
50 phr	3.5	10.1	217	79.2

^a t_i : the exothermic initial times.

^b t_p : the exothermic peak times.

^c ΔH_I : heat of reaction at isothermal temperature.

Table III Glass Transition Temperatures of Epoxy and PPO Phases of Epoxy/PPO System in Cured States

PPO Content in Blend	T_g of Cured Blend ($^{\circ}\text{C}$) ^a	
	PPO Phase	Epoxy Phase
0 phr	—	134
10 phr	194	134
20 phr	195	132
30 phr	198	132
40 phr	200	128
50 phr	200	—

DMA measurement, ramp: $5^{\circ}\text{C}/\text{min}$ from 50°C to 250°C at 1 Hz. Cure condition: 4 h at 180°C followed by 4 h at 220°C .
^a T_g of PPO: 220°C .

Morphology of Cured Materials

The epoxy/PPO mixture exhibited a typical upper critical solution temperature (UCST) phase behavior.¹⁸ Figure 1a shows that at the early stage of curing, the mixture (50 phr PPO) was homogeneous at the cure temperature (180°C UCST). After 5 min of cure time, the fracture surface displayed two grossly separated domains, i.e., the PPO-rich phase and the epoxy-rich domains (Fig. 1). However, it was still difficult to distinguish discontinuous from continuous domains. As the cure continued to 10 min, the PPO-rich domain was clearly mesh-like and interconnecting, and thus continuous (Fig. 1[c]). The increase in the molecular weight of the epoxy caused the UCST shift to higher temperatures. Then the system was thrust into the two-phase regime, and the phase separation took place via spinodal decom-

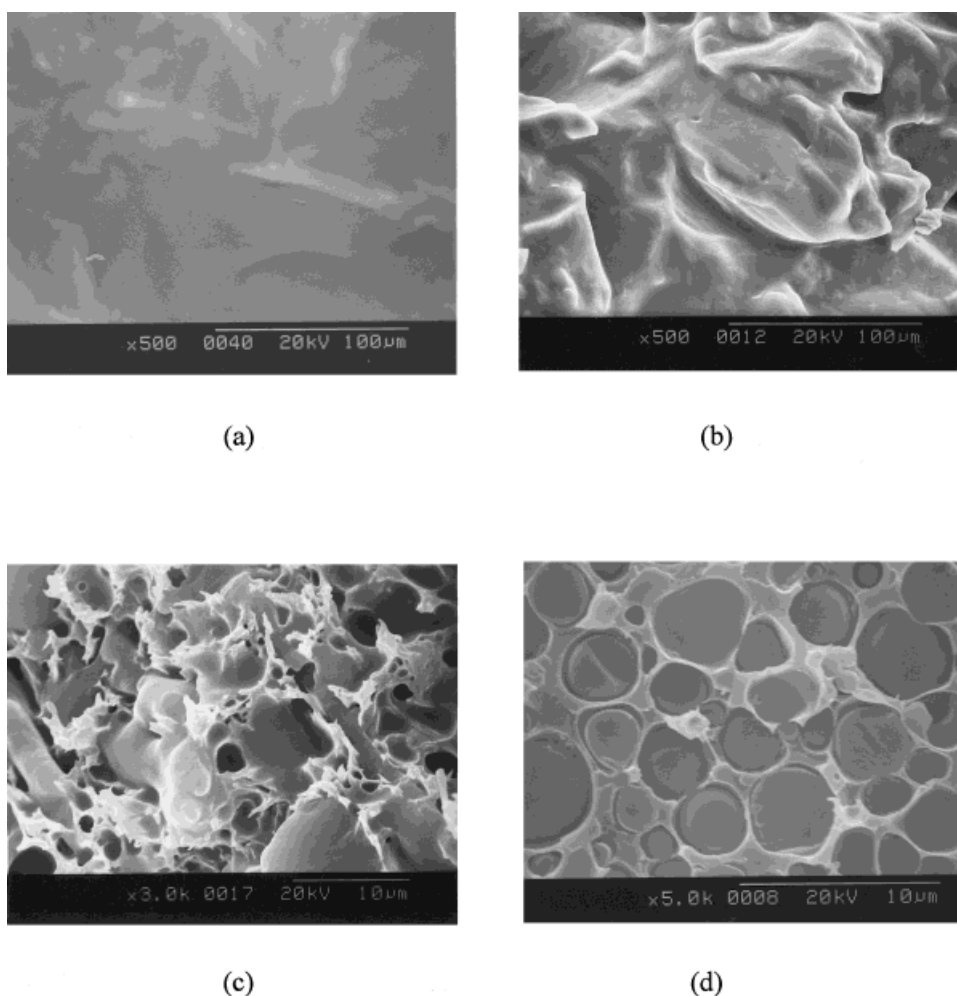


Figure 1 Scanning electron micrographs of 50 phr PPO/epoxy blend specimens cured for different times at 180°C : (a) 30 s; (b) 5 min; (c) 10 min; (d) 30 min.

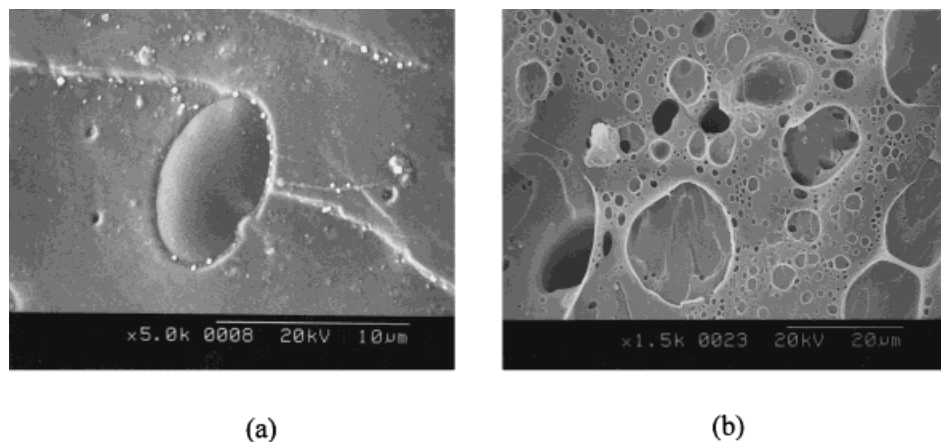


Figure 2 Fracture surfaces of 10 phr PPO/epoxy blend specimens: (a) nonetched; (b) solvent-etched.

position (SD).^{19,20} As expected from the SEM observations, the cured material had the two-phase morphology fixed at the late stage of SD. One can see spherical domains of epoxy resin dispersed quite regularly in PPO matrix (Fig. 1[d]).

The morphology of the final cured epoxy/PPO blends was found to be dependent on the content of PPO. SEM inspection of the fracture surface of broken specimens revealed that large and small PPO-particles were present especially at a low PPO content (<30 phr). The fracture surface of the 10 phr PPO blend (Fig. 2[a]) consists of a continuous epoxy matrix with the PPO-rich domain clearly existed as fine dispersed particles. After soaking the fracture surface in dichloromethane, we found that the particulate phase had dissolved, which indicated a lack of signifi-

cant cross-links in PPO (Fig. 2). Figure 3 shows the etched and nonetched SEM of the epoxy/PPO (30 phr) blend after cure. There are regions of phase inversion, and there is also a pronounced skin of continuous epoxy phase, which means partial phase inversion took place in the epoxy/PPO (30 phr) blend. The 50 phr PPO blend (Fig. 1[d]) shows complete phase inversion and has a honeycomb morphology. The epoxy domains (5 μm in diameter) are connected by threads of PPO. The morphology of epoxy/PPO blends changed from a continuous epoxy/discrete PPO pattern at low PPO contents (10 phr or lower) to an epoxy domains wrapped in layers of thermoplastic at a PPO content of 50 phr, or higher.

To improve the miscibility, three TAIC concentrations were evaluated as possible surfactant for

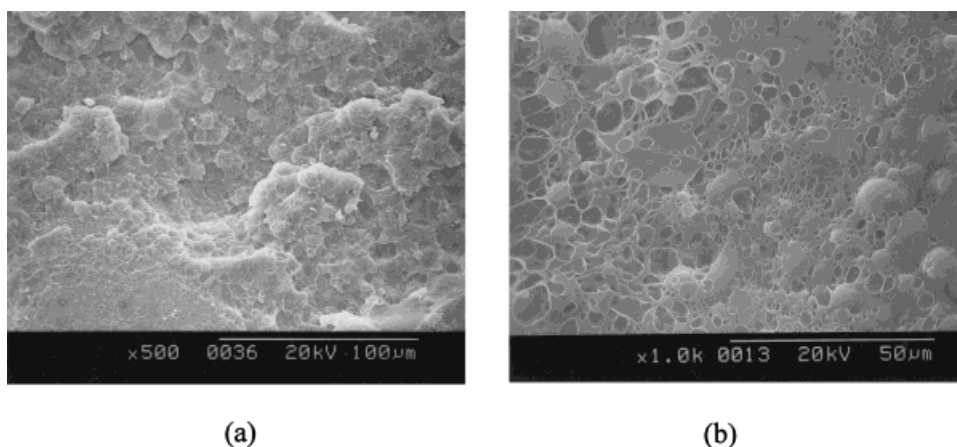


Figure 3 Fracture surfaces of 30 phr PPO/epoxy blend specimens: (a) nonetched; (b) solvent-etched.

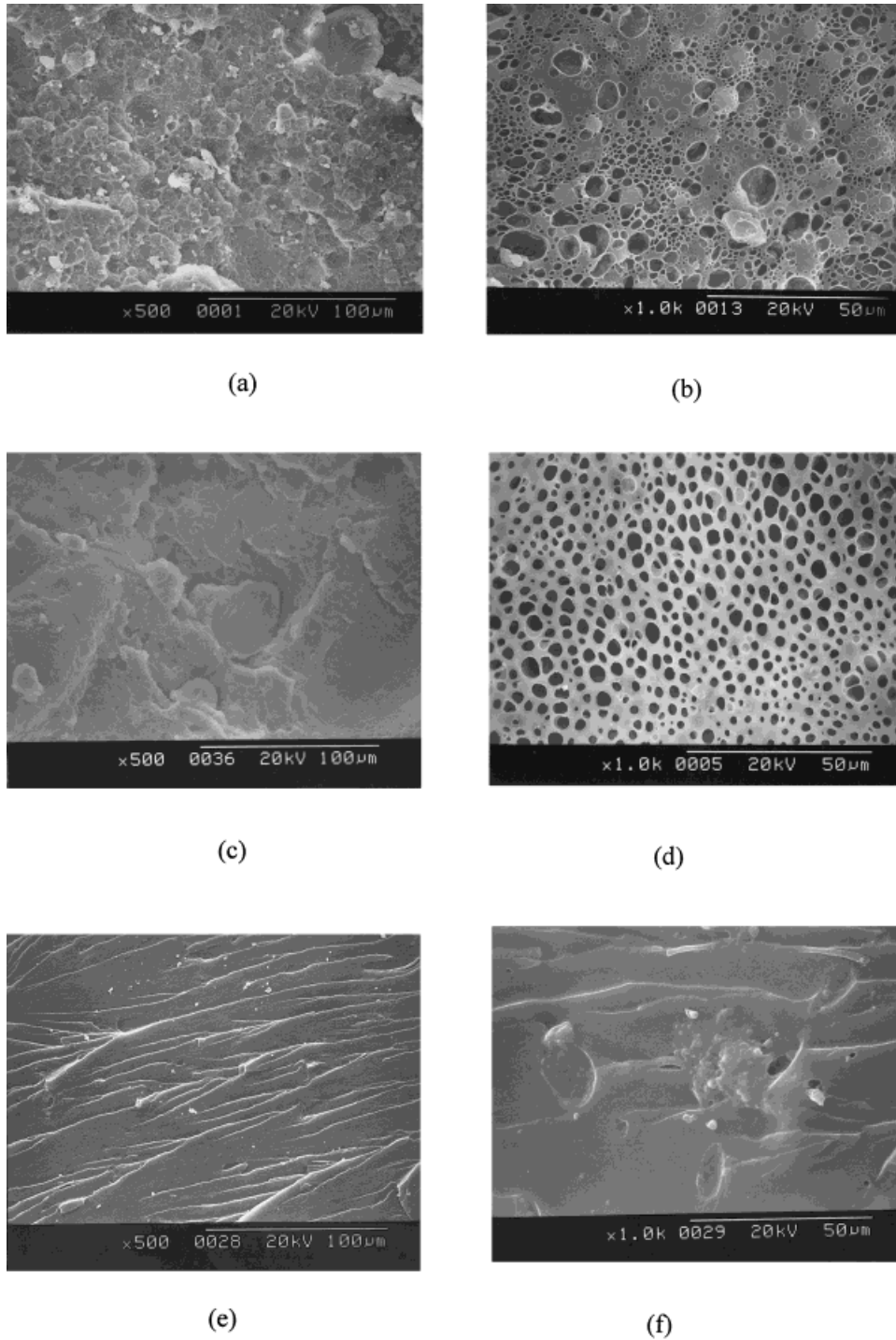


Figure 4 Scanning electron micrographs of 30 phr PPO/epoxy blends with various TAIC content: (a) 5 phr TAIC; (b) 5 phr TAIC (etched); (c) 10 phr TAIC; (d) 10 phr TAIC (etched); (e) 20 phr TAIC; (f) 20 phr TAIC (etched).

PPO-modified epoxies. Figure 4 shows the dichloromethane etched and nonetched SEM morphologies of the epoxy/PPO (30 phr) blends with various TAIC content. The visible and distributed

holes correspond to PPO phase as this is the minor component in epoxy-rich phase. The noncompatibilized blend (Fig. 3) has the largest PPO domain size in epoxy-rich phase. The size of the

PPO phase decreases with the increase of TAIC content (Fig. 4). SEM shows that the morphology of epoxy/PPO (30 phr)/TAIC (20 phr) blend seems miscible because TAIC is miscible in epoxy, and the PPO chains are bound to TAIC network. A further contributory cause for the miscibility of blends could be the restriction of phase separation via SD, which was delayed by the incorporation of graft copolymer. The formation of graft copolymer in PPO/TAIC is conceivable because the methyl group of PPO is easily attacked by radical from TAIC.²¹ The bound PPO chain is difficult to be extracted with a good solvent of PPO.

Dynamic Mechanical Analysis

The temperature dependence of the dynamic mechanical analysis (DMA) for polymer blends as a function of composition yields particular insight into the structure of semicompatible polymers. The DMA result in Figure 5 ([a] and [b]) clearly show the two-phase character and partial mixing took place in the cured epoxy/PPO system; two-step decrease in dynamic storage modulus E' and two $\tan \delta$ peaks with increasing temperature. Thermoplastic PPO undergoes its glass transition, resulting in a much larger change in E' as the material softens from a plastic to viscoelastic property, which corresponds to the onset of long-range coordinated motion, and $\tan \delta$ peak exhibits a sharp damping peak. But in the epoxy/PPO blends, the modulus drops at a lower rate, and the rubbery plateau modulus of the cured materials above the T_g of PPO is kept at a high level. It implies that the entanglements consist of PPO chains looping around the epoxy network, and thus the molecular motion becomes more restricted. As the PPO content increases, the morphology of the blends changed to a dispersed epoxy particles in a continuous PPO matrix, and the storage modulus of a higher PPO content blend shows only one much more obvious transition near the PPO glass transition region. The value of the storage modulus in the plateau region between the two-glass transition depends on the ratio of the components and on which phase tends to be the continuous phase and which is the dispersed phase.

The PPO-rich and epoxy-rich $\tan \delta$ peak height in the blend are lower than those in neat PPO and epoxy resin because of the interpenetrating effect. Chains or segments of PPO close to a relatively glassy epoxy network tend to have restricted mo-

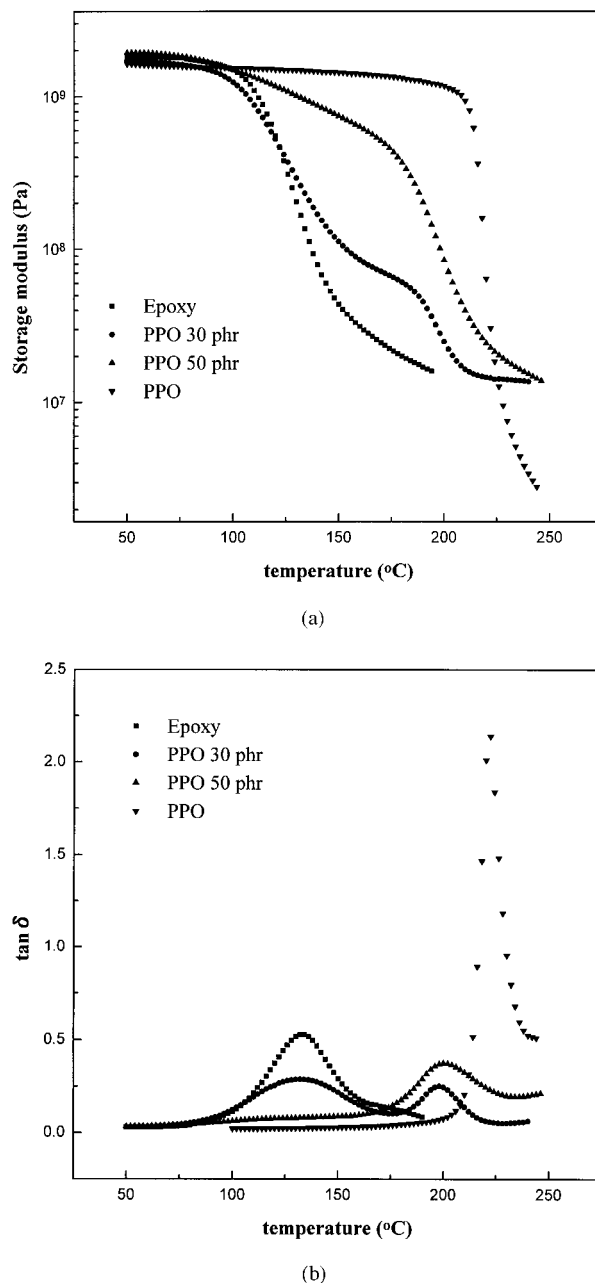


Figure 5 (a) Dynamic storage modulus (E') in the temperature range of 50–250°C for the epoxy/PPO blends. (b) Relaxation peaks ($\tan \delta$) in the temperature range of 50–250°C for the epoxy/PPO blends.

tion at the temperature for neat PPO and epoxy relaxation. The variation in $\tan \delta$ peak height correlates with the amount of the continuous phase present. The PPO-rich $\tan \delta$ peak height increases with the increasing PPO resin content, and the damping peak of epoxy almost disappeared, at which PPO becomes the continuous phase. Thereafter, the damping characteristics of

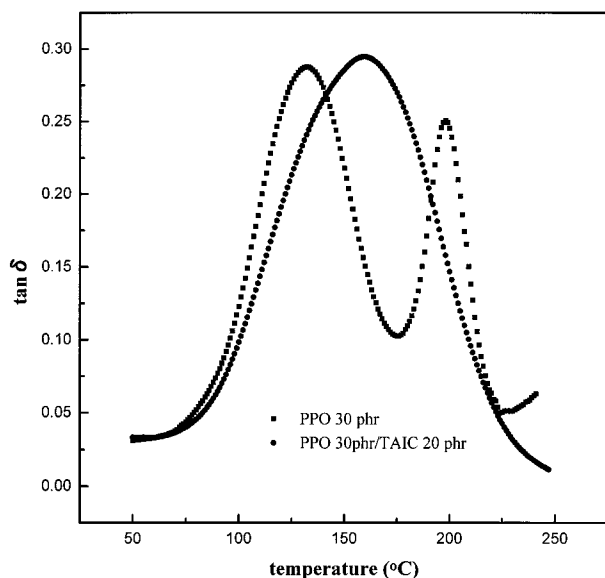


Figure 6 Relaxation peaks ($\tan \delta$) of epoxy/PPO (30 phr) blend and of epoxy/PPO (30 phr) blend with 20 phr TAIC.

PPO-rich phase should dominate and increase in $\tan \delta$ peak height should ensue with increasing PPO content. $\tan \delta$ peak height may be used as convenient indicator of the morphological state of the phases within a blend.

Figure 6 shows the $\tan \delta$ vs. temperature for the epoxy/PPO (30 phr) blend with 20 phr TAIC content. The T_g of PPO-rich phase in the epoxy/PPO (30 phr) blends is located around 200°C and is found to decrease with increasing TAIC content. When using 20 phr TAIC as the component of blend, two $\tan \delta$ peaks shifted inward in the T_g of the two phase, its shape became broader and showed only one peak. The broadness of the α relaxation indicates the complexity of the blend structure, based on PPO incorporating into the TAIC network. The observed T_g decrease for the PPO/TAIC rich phase may be attributed to the in situ-formed TAIC-PPO copolymer and the partial miscibility between epoxy and TAIC-PPO copolymer.

Mechanical and Dielectric Properties

Tensile modulus and strength at room temperature is plotted against PPO concentration in Figure 7. Over the composition range studied, the modulus shows a slight decrement from 4.0 GPa in the epoxy resin to 3.7 GPa in a blend containing 50 phr of PPO, and the tensile strength shows a slight increment from 68 to 72 MPa. Although there are wide variations in morphology and degree of phase sep-

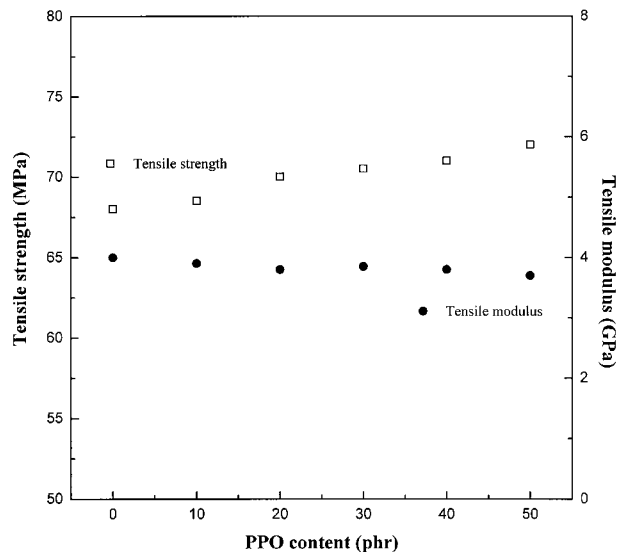


Figure 7 The tensile modulus and strength as a function of blend composition for the epoxy/PPO system.

aration, the tensile strength and modulus vary only within a very narrow range. The critical strain-energy release rate (G_{IC}) of the epoxy/PPO blends, as expected, increased with increasing PPO content (Fig. 8). Although the addition of 10 phr PPO only gives small improvement in fracture properties, increasing the PPO content more than 20 phr results in a significant increase in toughness. The relation between PPO content and fracture toughness is due to the morphology of the blend, which undergoes a

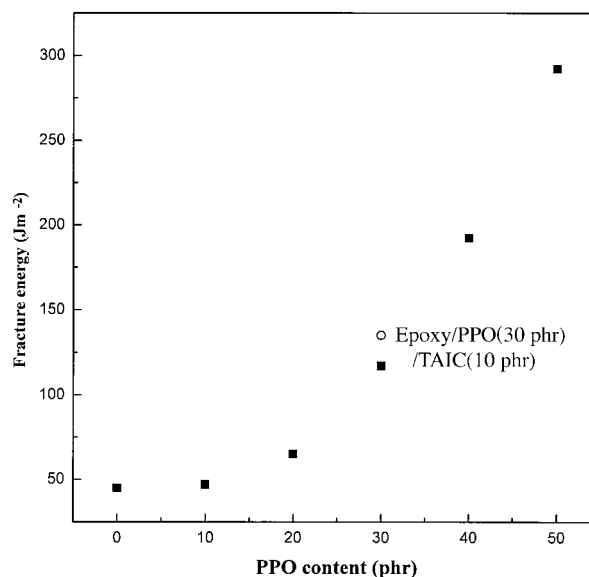


Figure 8 The fracture energy (G_{IC}) as a function of blend composition for the epoxy/PPO system.

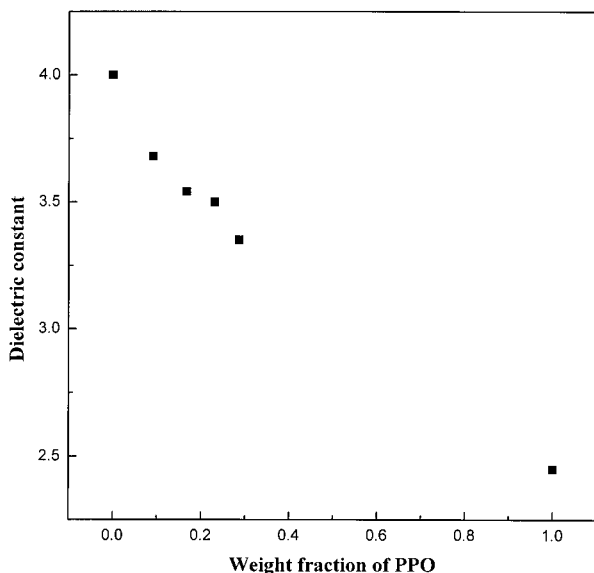


Figure 9 Dielectric constant as a function of blend composition for the epoxy/PPO system.

dramatic change from a discrete PPO/continuous epoxy pattern at low PPO content to an epoxy domain wrapped in layers of thermoplastic at high PPO content. Thus, yielding of the PPO continuous phase is the main toughness mechanism. Furthermore, the fracture toughness of the TAIC-modified system also was found to be slightly improved by adding TAIC.

In dielectric analysis, PPO has a superior dielectric constant of 2.45 at 1 MHz. Compounding of PPO with epoxy resin improved dielectric properties of the material. The dielectric constant of the blend decreased with PPO content in a linear fashion (Fig. 9).

CONCLUSIONS

The following conclusions may be drawn from the results of this study. (a) An autocatalytic mechanism was observed for cyanate ester-cured epoxy/PPO blends over a range of compositions. Although the reaction mechanism of the blends remained the same as that of the neat epoxy, the cure reaction of the blends were more reactive at lower temperatures than the latter, and the heat of reaction decreased with increase in PPO content; (b) SEM and DMA may be used to study the phase separation of PPO from solution in epoxy resin. All the blends exhibited heterogeneity, and their morphology was found to be dependent on the content of PPO. Phase inversion occurs when PPO content is 20 phr or higher; (c) DMA indi-

cates that partial mixing took place exist in all the mixtures, but the degree of miscibility of the epoxy/PPO blends depends on the cross-linking density of the epoxy. In our other experiment, low cross-linking density epoxy of the blends caused the $\tan \delta$ peak of the PPO-rich phase shifted to lower temperature; (d) The tensile strength and modulus vary only within a narrow range in the blends. In contrast, there is a significant increase in toughness when PPO forms the continuous phase. The obvious improvement in fracture properties appears to arise from ductile tearing of the PPO; (e) The dielectric constant of the blend decreased with PPO content in a linear fashion; (f) Addition of TAIC to the epoxy/PPO system can eliminate the occurrence of the large PPO particles in the blends. SEM and DMA showed the improvement of miscibility and solvent resistance in the TAIC-modified systems.

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