

# Reaction Mechanisms, Microstructure, and Fracture Properties of Thermoplastic Polysulfone-Modified Epoxy Resin

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## SYNOPSIS

The microstructure and fracture properties of diglycidyl ether of bisphenol A (DGEBA) epoxy resins modified with phenolic hydroxyl-terminated polysulfone (PSF) and cured with diaminodiphenyl sulfone (DDS) hardener have been investigated as a function of the molecular weight and concentration of PSF. The microstructure changed from a typical particulate structure to a phase-inverted structure as the molecular weight and/or the concentration of the modifier increased. The fracture toughness, measured by compact tension tests, increased with the microstructural changes toward the phase-inverted structure. The microstructural changes observed have been interpreted in terms of variation in the reaction mechanisms as determined by near-infrared spectroscopy. The level of minor reactions such as etherification and homopolymerization reactions increased with increasing molecular weight and/or concentration of the modifier, in line with the tendencies observed in microstructure and fracture toughness. In the system containing 20 wt % of  $M_n$  10,000 PSF, about 30% of the epoxy groups were consumed by etherification and homopolymerization reactions, whereas none of these reactions occurred in the unmodified system. The increase in minor reactions in the modified systems may be due to the restricted molecular mobility, resulting from the increase of system viscosity caused by the modification. This increase in viscosity also reduced the rate of phase separation. The degree of heterogeneity in the epoxy network must increase with the increasing side reactions. The formation of the heterogeneous epoxy network and the slowdown of phase separation will prevent a uniform precipitation of the modifier and finally result in a heterogeneous partially phase-inverted structure or the completely phase-inverted structure, depending on the amount of modifier incorporated over the critical concentration. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The incorporation of ductile thermoplastic oligomers into epoxy resins has been used as an alternative to rubber modification as a method for improving the intrinsically poor fracture properties of highly cross-linked epoxy resins. This improvement in fracture toughness is achieved without sacrificing other useful properties such as high glass transition temper-

atures, modulus, and chemical resistance, which are compromised by rubber modification.<sup>1-8</sup>

The observed microstructures of thermoplastic-modified epoxy resins are not markedly different from those of similar rubber-modified epoxy resins.<sup>3,4,7</sup> It has been found that the microstructure is influenced by material parameters such as the reactant ratio,<sup>9-11</sup> concentration and type of the modifier,<sup>12-18</sup> and cure conditions.<sup>19-24</sup> The thermodynamic compatibility and the system viscosity between the onset of the phase separation and the gelation have been studied to determine the resultant microstructure in the modified resin systems.<sup>25,26</sup> The phase-inverted co-continuous struc-

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ture, which is observed with high loading of the modifier (over 20%) and which has interconnected globular epoxy particles in a thermoplastic matrix, has attracted much interest because it usually gives high fracture toughness. Yamanaka et al.<sup>27,28</sup> observed the phase-inverted co-continuous structure by decreasing cure temperature in their rubber- and polyether sulfone-modified resin systems. They reported that the decrease of cure temperature slowed down the rate of phase separation (based on the spinodal decomposition process) without significantly reducing the rate of chemical reaction. This arrested the structure at an early stage of phase separation and finally resulted in interconnected globular epoxy particles in a co-continuous, modifier-rich matrix.

In this article, we employed the phase-separation model by Yamanaka et al.<sup>27,28</sup> in addition to the reaction mechanism for the formation of the epoxy network studied by near-infrared spectroscopy in order to interpret the variation in microstructures observed with varying molecular weight and concentration of the modifier in PSF-modified resin systems.

## EXPERIMENTAL

### Materials and Sample Preparation

A diglycidyl ether of bisphenol-A epoxy resin (Epikote 8283, Shell Chemicals,  $M_n$  380) and an aromatic amine curing agent, 4,4'-diaminodiphenyl sulfone (Anchor Chemicals,  $M_n$  248), were used as the primary matrix materials. Two phenolic hydroxyl-terminated polysulfones of  $M_n$  6400 and 10,000, used as modifiers, were synthesized from bisphenol A and dichlorodiphenyl sulfone monomers, by the conventional method described by Merriam and co-workers.<sup>29,30</sup> The desired molecular weight of the final product was obtained by varying the molar ratio of reactant monomers according to the modified Carother equation.<sup>31</sup> The polysulfone-modified mixtures, containing a stoichiometric amount of DGEBA to DDS based on the functionality of the two monomers, and different levels (5–20 wt %) of polysulfone, were prepared in a two-step process. The DGEBA and PSF monomers were first pre-reacted at 140°C under vacuum in the presence of a catalyst (tetramethylammonium hydroxide) prior to adding DDS in order to induce chemical bonding, and then DDS was added to the pre-reacted DGEBA/PSF mixture. The weight percent of PSF incorporated was calculated from the following relationship:

$$\text{Wt \% of PSF} = \frac{W_3}{W_1 + W_2 + W_3} \times 100\% \quad (1)$$

where  $W_1$ ,  $W_2$ , and  $W_3$  are the weights of DGEBA, DDS, and PSF monomers added into the system, respectively.

The prepared mixtures were poured into a Teflon mold and cured in an air oven at 140°C for 2 h and then again for 2 h at 180°C. These cured bars (120 × 12 × 16 mm) were machined and used for mechanical and near-infrared spectroscopic tests. Some of the machined samples were further postcured at 205°C for 3 h and used for comparative studies of the degree of cure relative to the nonpostcured samples.

### Testing Techniques

The infrared absorption spectra of the cured epoxy resins were recorded by an Alpha Centauri FTIR spectrometer (Mattson Instruments Inc, U.S.A.) in the near-infrared region. The chemical conversions of epoxy and primary and secondary amine groups were obtained by analyzing the spectra according to the quantitative analysis method reported in our previous paper.<sup>32</sup>

The mechanical tests were carried out on a testing machine (Instron 4505) at room temperature. At least five samples were tested for each cure condition. The fracture toughness tests were carried out at a crosshead speed of 1.0 mm/min. Small compact tension specimens (15.8 × 15.2 × 10 mm) were pre-cracked by inserting a thin razor blade into the machined notch and impacting with a small hammer. To prevent crack blunting, a fresh razor blade was used for each specimen. The flexural modulus was measured on rectangular specimens of 50 × 10 × 2.4 mm in three-point bending mode at the same crosshead speed as used in the compact tension tests; the span to depth ratio was 16 : 1.

Solvent uptake was measured gravimetrically after immersing the samples in methyl ethyl ketone (MEK) at room temperature for 30 days. The fracture surfaces were examined on a Jeol JSM-840A scanning electron microscope (SEM) at 15 kV. Prior to the examination, the surfaces were gold-coated using a high-vacuum gold sputterer to improve the conductivity.

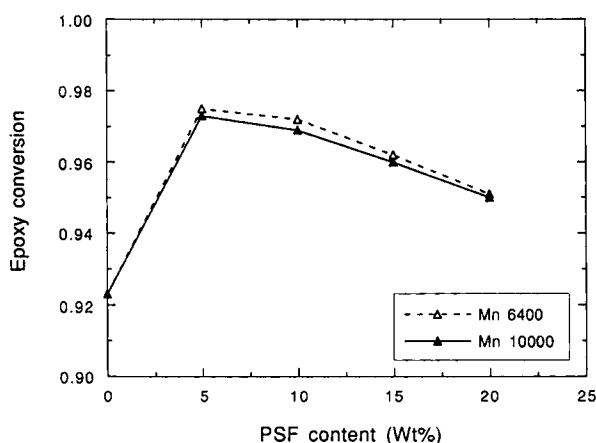
## RESULTS AND DISCUSSION

### Reaction Mechanisms

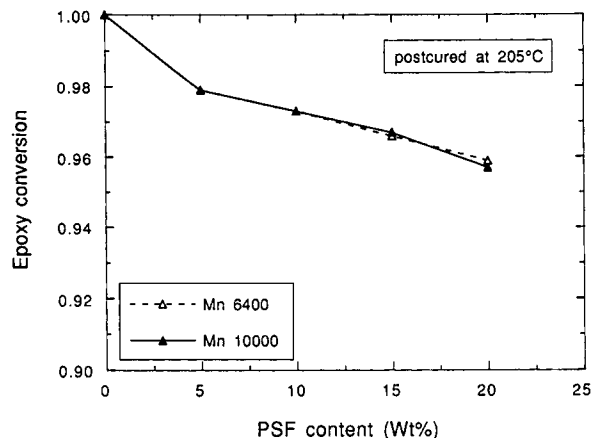
Theoretically, a maximum of 1.96% of epoxy groups could be consumed by the reaction with hydroxyl

groups of PSF in 20 wt % of an  $M_n$  6400 PSF-modified system. It is reasonable to expect that at lower concentrations of PSF the amounts of epoxy consumed by the reaction with PSF would be proportionately lower.

The chemical conversions of the cured samples, obtained by measuring the epoxy group consumption by quantitative assessment of the near-infrared absorption band at  $4535\text{ cm}^{-1}$ , are shown in Figures 1 and 2 as a function of molecular weight and concentration of PSF. In the two-step cure samples, shown in Figure 1, the conversion was lowest at 0 wt % of PSF and highest at 5 wt % of PSF and then decreased with increasing concentration of PSF. When the samples were further postcured at higher temperature, the conversions were not changed noticeably except that of the unmodified sample, which increased to 100% conversion as shown in Figure 2. It was notable that the molecular weight of PSF had no effect on the degree of conversion. From the increase of conversion by postcure in the unmodified sample, it can be inferred that the final cure temperature of  $180^\circ\text{C}$  was not high enough to obtain a full cure. This observation agrees with our previous results (obtained in the study of the influence of the cure temperature on unmodified resin systems<sup>19</sup>) in that the maximum conversion can be achieved only when the final cure temperature employed is near or over the  $T_{g\alpha}$  ( $205^\circ\text{C}$ ) of the system. No change in conversion by postcure in the modified samples suggests that the chemical reactions are terminated earlier in the modified system than in the unmodified system. The decrease of the maximum conversion with increasing concentration of PSF may be attributed to the restricted (diffusion-controlled) re-



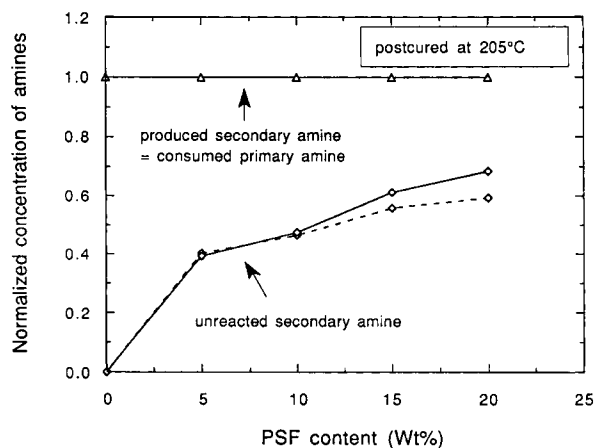
**Figure 1** Epoxy conversion (from NIR band at  $4535\text{ cm}^{-1}$ ) vs. PSF content for PSF-modified DGEBA/DDS samples. Cure schedule was  $140^\circ\text{C}$  2 h/ $180^\circ\text{C}$  2 h.



**Figure 2** Epoxy conversion (from NIR band at  $4535\text{ cm}^{-1}$ ) vs. PSF content for postcured samples. Cure schedule was  $140^\circ\text{C}$  2 h/ $180^\circ\text{C}$  2 h/ $205^\circ\text{C}$  3 h.

action caused by viscosity increases in the modified systems.

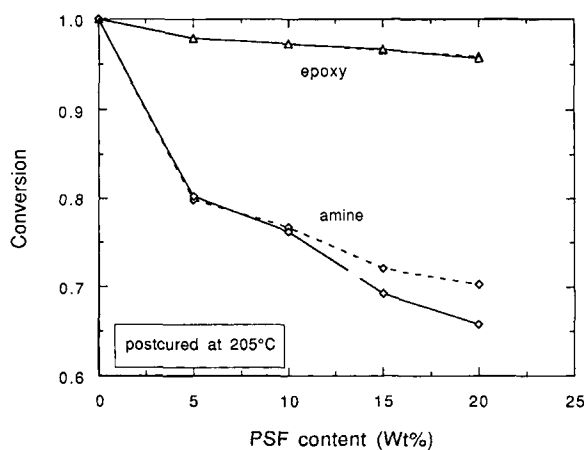
The concentrations of the primary and secondary amine groups were obtained by measuring the corresponding infrared band areas and are shown in Figure 3. It was noted that the primary amine groups were completely consumed in all samples prepared in this study. The concentration of produced secondary amine was estimated from the consumption of the primary amine; for each reaction of a primary amine, one secondary amine is produced. However, not all the secondary amine groups reacted in the



**Figure 3** Normalized concentration of amine groups (from NIR band at  $5012\text{--}5077\text{ cm}^{-1}$  for  $\text{NH}_2$  and at  $6577\text{--}6692\text{ cm}^{-1}$  for  $\text{NH}$ ) vs. PSF content for DGEBA/DDS samples modified with  $M_n$  (---) 6400 and (—) 10,000 PSF. Cure schedule was  $140^\circ\text{C}$  2 h/ $180^\circ\text{C}$  2 h/ $205^\circ\text{C}$  3 h. ( $\Delta$ ) Produced secondary amine; ( $\diamond$ ) unreacted secondary amine.

modified samples. In fact, the concentration of the unreacted secondary amine at the end of the cure increased with increasing concentration of PSF, as shown in Figure 3. The comparison of conversions of the epoxy and amine (sum of the primary and secondary amine) groups, plotted in Figure 4, reveals a substantial discrepancy between the consumption of epoxy and amine. This indicates that the consumption of epoxy by reactions with nonamine groups increases rapidly with the incorporation of even 5 wt % PSF and further increases with increasing concentration of PSF. At 20 wt % of  $M_n$  10,000 PSF, about 30% of epoxy groups appear to be consumed by side reactions. This calculation is based on the assumption that the amine groups themselves can react only with epoxy groups.

The molecular weight of PSF does not appear to affect significantly the amount of the side reaction. The most likely side reactions in such modified systems are either the etherification reactions that occur between epoxy and hydroxyl groups or the homopolymerization reaction of the epoxy groups or both.<sup>33-35</sup> It is possible that the increase in nonamine reactions in the PSF-modified systems is due to a greater increase in the viscosity of the matrix resin caused by faster molecular weight increases when the relatively large PSF molecules are incorporated into a reacting chain. In this argument, the rates of reaction of the secondary amine groups (which have to be buried within the main polymer chain) with



**Figure 4** Conversions of ( $\Delta$ ) epoxy group (replotted from Fig. 2) and ( $\diamond$ ) amine group (calculated from Fig. 3) vs. PSF content. DGEBA/DDS modified with  $M_n$  6400 (---) and (—) 10,000 PSF. Cure schedule was 140°C 2 h/180°C 2 h/205°C 3 h. The divergence of conversion between epoxy and amine groups indicates the level of side reactions.

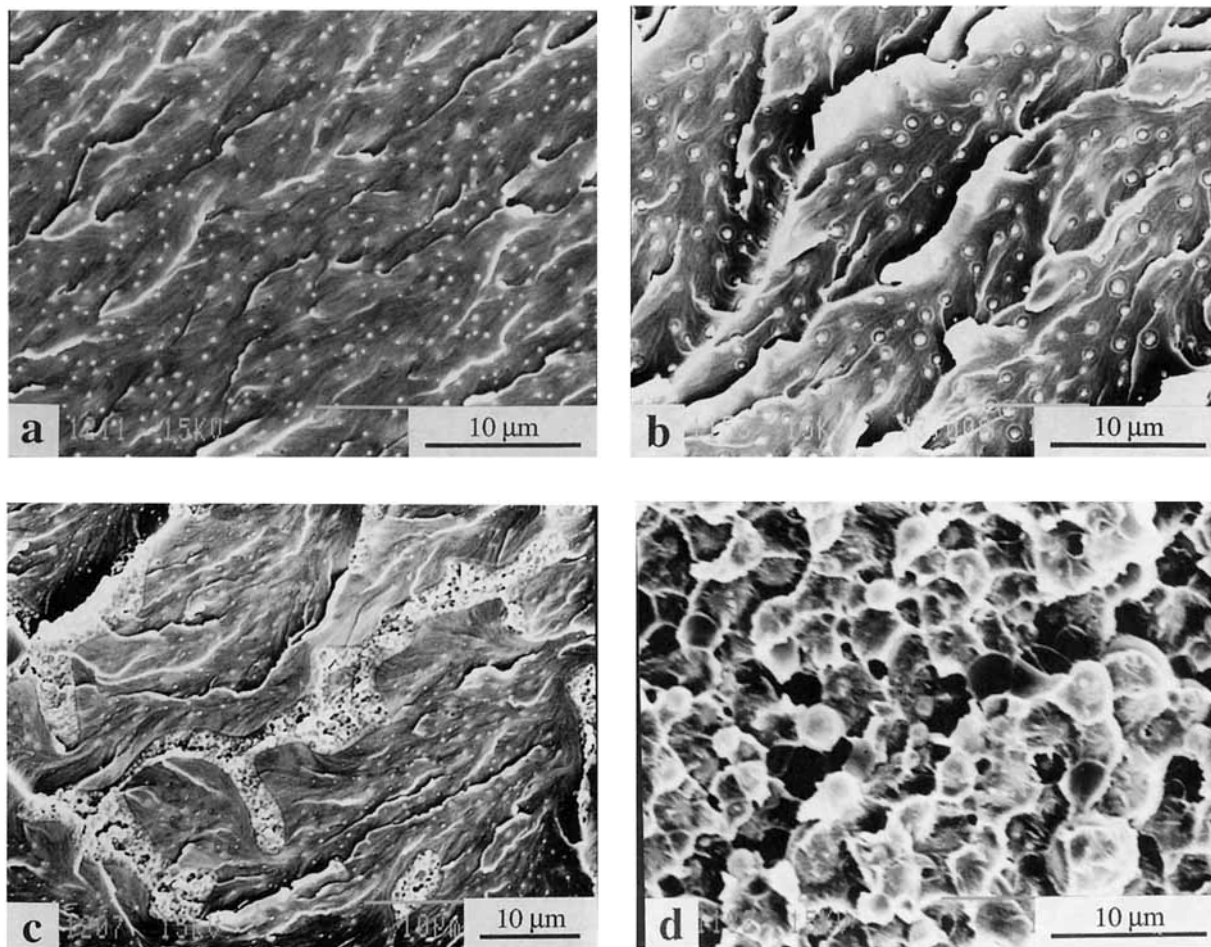
the epoxy groups are retarded more by the system viscosity increase than are those of the epoxy/epoxy reactions where both groups are at the chain ends. Another possible effect that could retard the amine reactions would be the selective complexing of the more polar groups with the sulfone groups in the PSF.

Finally, we can reach the conclusion that the changes in the epoxy network of the modified systems (due to etherification and homopolymerization reactions) are either or both of the following: (i) an increase of molecular weight between cross-links caused by the homopolymerization reaction, and/or (ii) the formation of ring structures by the intramolecular etherification reaction. We can expect from this result that the degree of heterogeneity of the epoxy network will increase with increasing degree of etherification and homopolymerization reactions.

### Microstructures

The SEM micrographs of the fracture surfaces of the modified systems, containing 5–20 wt % of  $M_n$  10,000 PSF, are presented in Figure 5(a)–(d). As can be seen from Figure 5, the microstructure changes from the typical particulate structure at 5 and 10 wt % of PSF to the partially phase-inverted structure at 15 wt % of PSF (considered as an intermediate structure of the particulate and completely phase-inverted structures) to the completely phase-inverted structure finally observed at 20 wt % of PSF loading.

In the samples containing particulate structures, the particle size increases with increasing concentration of PSF from 5 to 10 wt %. This is quite consistent with the result reported by Hedrick et al.<sup>36</sup> in the similar modified resin system with slightly different molecular weight PSF ( $M_n$  5300 and 9700). The micrograph for 20 wt % of PSF is also shown in Figure 6 in higher magnification. In this picture can be seen the ductile torn matrix surrounding the nearly closely packed globular hard particles. To identify the PSF phase in the particulate and phase-inverted structures, the fractured surfaces were etched by methyl ethyl ketone (MEK). The unmodified PSF is quite soluble in MEK, whereas the cured epoxy is not. This allows differential etching from the surface. The micrographs of the etched surfaces are presented in Figure 7. The particles seen in Figure 5(b) are not observed in Figure 7(a), implying that they are a PSF-rich phase. On the other hand, in the micrograph of the etched surface of the phase-inverted structure shown in Figure 7(b), the

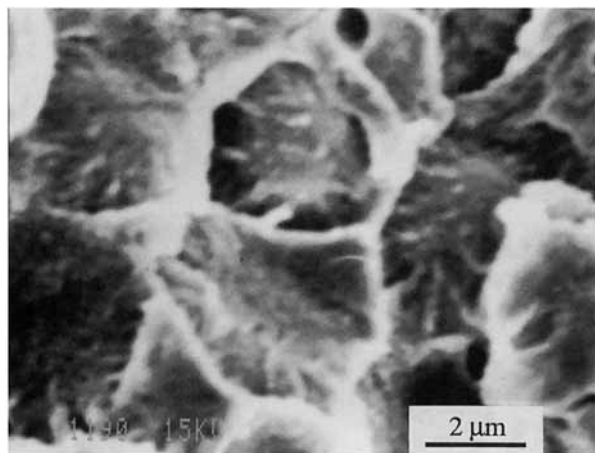


**Figure 5** SEM micrographs of the fracture surfaces of  $M_n$  10,000 PSF-modified DGEBA/DDS systems. The amounts of PSF incorporated into the systems are (a) 5, (b) 10, (c) 15, and (d) 20 wt %.

ductile torn matrix (observed in Fig. 6) was dissolved and precipitated onto the hard particles. This etching approach for the identification of PSF gives strong support to the view that (i) the particles in the particulate structure are a PSF-rich phase dispersed in the epoxy-rich matrix, and (ii) the interconnected particles in the phase-inverted structure are an epoxy-rich phase surrounded by a continuous PSF-rich matrix.

The partially phase-inverted structure shown in Figure 5(c) has rarely been reported in the literature, although the completely phase-inverted structure has been more extensively described due to the high fracture toughness that accompanies this structure. Yamanaka et al.<sup>27,28</sup> observed a phase-inverted co-continuous structure by decreasing cure temperature in their rubber- and polyether sulfone (PES)-modified epoxy systems (containing over 30

phr [approximately 20 wt %] of modifier). We also observed the variation of the microstructure with varying cure temperatures.<sup>37</sup> Yamanaka et al. indicated that a decrease in cure temperature slowed down the rate of phase separation (through the spinodal decomposition process) without significantly reducing the rate of chemical reaction and arrested the structure at an early stage of phase separation, resulting in interconnected globular epoxy particles in a co-continuous (modifier-rich) matrix. Based on our observations and the results of Yamanaka et al., we conclude that the influence of the concentration of the modifier and that of cure temperature on the rate of phase separation are similar. Both of them reduce the rate of the phase separation through the increase of the system viscosity. In addition, we observed an increase in the degree of the etherification and homopolymerization reactions with increasing



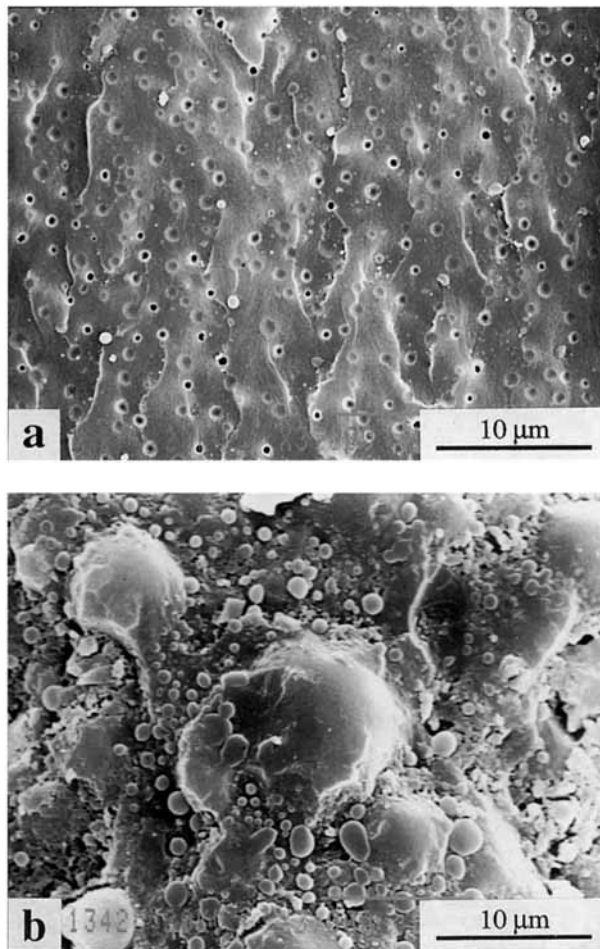
**Figure 6** SEM micrograph of the phase-inverted region of 20 wt % of  $M_n$  10,000 PSF-modified DGEBA/DDS system in high magnification ( $\times 10,000$ ), showing a ductile torn continuous PSF matrix surrounding hard epoxy particles.

concentration of PSF and propose that these reactions are enhanced by the reduced mobility of the system, resulting in a heterogeneous network. These two combined effects (i) of the slowdown of phase separation and (ii) of the increase of the heterogeneity during phase separation are considered to be the main factors causing the heterogeneous partially inverted structure (or the completely phase-inverted structure) depending on the concentration of PSF over the critical concentration (15 wt % in this study). The above observations support our conclusion that the system viscosity, which is influenced by the concentration of the modifier as well as the cure temperature, determines the phase-separation rate and the degree of the etherification and homopolymerization reactions (heterogeneity of network) and these complex effects may result in the phase inversion.

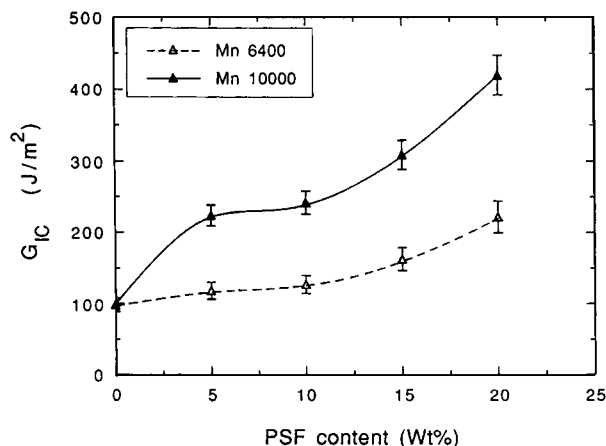
### Mechanical Properties

The variation of fracture toughness in terms of the strain energy release rate,  $G_{IC}$ , as a function of the molecular weight and the concentration of PSF is shown in Figure 8. The fracture toughness of a low molecular weight ( $M_n$  6400) PSF-modified system does not vary noticeably with the variation in PSF concentration. Even at 20 wt %, the maximum fracture toughness of the low molecular weight PSF-modified system is lower than the fracture toughness of the 5 wt % high molecular weight ( $M_n$  10,000)

PSF-modified system. Meanwhile, the fracture toughness of the high molecular weight PSF-modified system increased rapidly with increasing concentration.<sup>36</sup> The increase of the fracture toughness is rapid in the regions between 0 and 5 wt % and 10 and 20 wt % PSF concentration. In these regions, we observed the transition of the microstructure from pure epoxy to particulate and from particulate to phase-inverted structures, respectively. These concurrent transitions in the microstructure and fracture toughness with increasing concentration of PSF suggest that the microstructure strongly influences the fracture toughness and, presumably, the phase-inverted structure is the optimum structure for achieving high fracture toughness. The toughening mechanisms in the modified epoxies, which



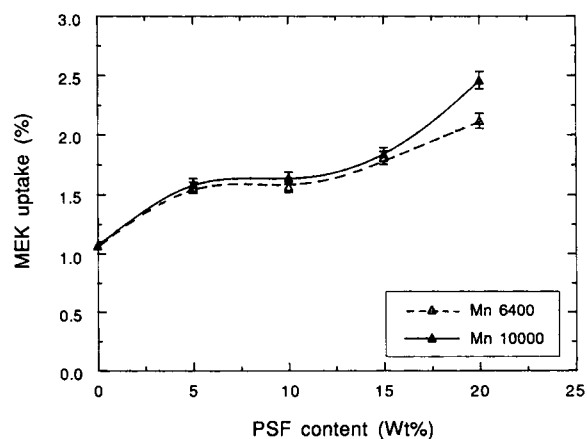
**Figure 7** SEM micrographs ( $\times 3000$ ) of the MEK-etched fracture surfaces of the PSF-modified DGEBA/DDS systems containing (a) 10 and (b) 20 wt % of  $M_n$  10,000 PSF.



**Figure 8** Plot of mode 1 critical strain energy release rate against PSF content for DGEBA/DDS systems modified with  $M_n$  6400 and 10,000 PSF. Cure schedule was 140°C 2 h/180°C 2 h.

lead to the above observed phenomena, are described in our separate publication.<sup>37</sup>

The solvent uptake as a function of molecular weight and concentration of PSF is shown in Figure 9. It is evident that an increase in the concentration of PSF reduces the solvent resistance significantly, whereas changes in the molecular weight of PSF are only significant at high PSF concentrations. However, it is believed that the solvent resistance may not be directly related to the various types of microstructure observed above for the following reasons: The solvent uptake of the modified resin systems may depend on both the free volume entrapped

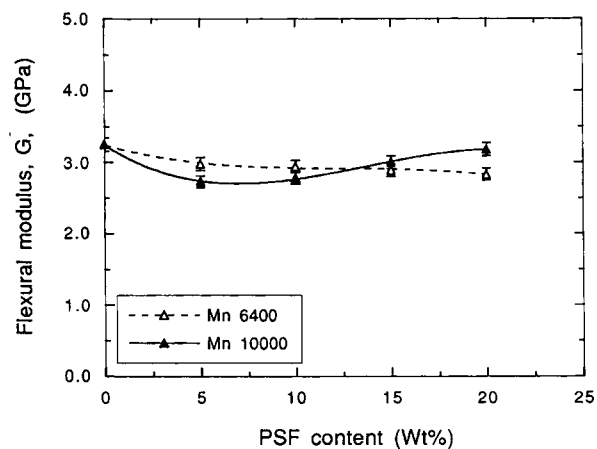


**Figure 9** Plot of solvent uptake against PSF content for DGEBA/DDS systems modified with  $M_n$  6400 and 10,000 PSF. Cure schedule was 140°C 2 h/180°C 2 h.

in the epoxy network and the intrinsic solubility characteristics of PSF. Both factors act toward increasing the solvent uptake as the concentration of PSF increases (free volume increases with increasing heterogeneity). Therefore, to properly understand the relationship between microstructure and solvent resistance, we believe that a single modified resin formulation needs to be used with all other material parameters fixed, and the microstructure can be changed with processing variables such as cure temperature. For example, in a separate study on the effect of cure temperature on the solvent resistance of a single PSF-modified resin system (containing 15 wt % PSF),<sup>38</sup> we observed an increase in solvent uptake with increasing cure temperature while the microstructure changed from the phase-inverted to the particulate structure. This result contrasts with the general literature results and implies that the solvent resistance is strongly dependent on free volume, not on the microstructure in single PSF-modified resin systems. We observed a similar free-volume dependence in unmodified resin systems.<sup>19</sup>

In summary, this observation allows us to reach the conclusion that the sacrifices of solvent resistance of epoxy resins that have been reported in the literature with thermoplastic or rubber modifications are not necessarily attributable to the microstructural variations, but more to the intrinsic solubility characteristics and concentrations of the incorporated modifiers.

The flexural modulus is shown in Figure 10. It can be seen that the modification by PSF does not



**Figure 10** Plot of the flexural modulus,  $G$ , against PSF content for DGEBA/DDS systems modified with  $M_n$  6400 and 10,000 PSF. Cure schedule was 140°C 2 h/180°C 2 h.

decrease the modulus noticeably in the range of this study. However, there are slight variations: The modulus of the low molecular weight PSF-modified system decreased slightly with increasing concentration of PSF. Meanwhile, the modulus of the high molecular weight PSF-modified system decreased at 5 wt % and then increased again up to the value of the unmodified system. The PSF used as a modifier in this study, unlike standard rubber modifiers, has a relatively high modulus at ambient temperature and, hence, the intrinsic modulus of an epoxy resin is not sacrificed noticeably by PSF modification as shown in Figure 10. The transition phenomenon observed at 5 wt % in high molecular weight PSF-modified system is not clearly understood but is believed to be due to the complex contributions of the stiffness of the epoxy network and the stiffness characteristics of PSF to the modulus of the system.

## CONCLUSIONS

The microstructure and fracture properties of diglycidyl ether of bisphenol A epoxy resins modified with phenolic hydroxyl-terminated polysulfones have been investigated as a function of the molecular weight and the concentration of the modifier. The microstructure changed from a typical particulate structure to a phase-inverted co-continuous structure as the molecular weight and/or the concentration of the modifier increased. The fracture toughness increased with microstructural changes from the particulate structure to the phase-inverted structure. The structural variation observed has been interpreted by means of the reaction mechanisms studied by near-infrared spectroscopy. The formation of the heterogeneous epoxy networks caused by the etherification and homopolymerization reactions and a reduced rate of phase separation were defined as the main factors determining phase inversion.

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