# Improvement of Thermomechanical Properties of a DGEBS/DDS System Blended with a Novel Thermoplastic Copolymer by Realization of a Semi-IPN Network

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**Abstract:** In this article we present the results of a study on the properties of a blend containing a 40:60 amine-ended copolymer, poly(ether sulfone)—poly(ether ether sulfone), with a system composed of diglycidyl ether of biphenol S and 4,4′-diaminodiphenyl sulfone (4,4′-DDS). Five formulations, which varied in amounts of modifier, were characterized through dynamic thermal mechanical analysis and fracture mechanics studies. The morphology of the blends was studied by transmission electron microscopy (TEM). The addition of thermoplastics enhanced the toughness of the system, resulting in an increase in the glass-transition temperature as a function of the amount of thermoplastics. No phase-separated morphology was detected by TEM analysis, leading to the conclusion that the formation of a homogeneous semi-IPN network occurred between the thermoplastics and the thermoset. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3021–3025, 2003

**Key words:** epoxy; semi-IPN, thermoplastic, viscoelastic properties, toughness

## INTRODUCTION

Epoxy resins are currently used as a matrix in advanced fiber-reinforced polymers (FRP) because of their superior thermal, mechanical, and corrosion-resistance properties. In the last decade the use of epoxy resins as a matrix for FRP required an enhancement of these characteristics; for that purpose, modifications by elastomers (rubbers) and engineering thermoplastic have been examined.

The modification of epoxy resins with reactive liquid elastomers such as carboxyl-terminated butadiene acrylonitrile rubber (CTBN) or crosslinked rubber particles could be successful in increasing the fracture toughness of brittle epoxy.[1–5] However, modification by adding low-temperature materials such as rubber resulted in a significant decrease in the modulus and the glass-transition temperature ($T_g$) of the treated resin. Recent studies confirmed a decay of the moisture resistance of epoxy systems modified by the addition of liquid reactive rubber.[6]

To overcome these problems, many attempts have been made to modify epoxy resin with high-performance engineering thermoplastics, characterized by a high $T_g$ and high toughness, such as polysulfone (PSF),[7,8] poly(ether sulfone) (PES),[9–11] poly(ether imide) (PEI),[12,13] and polyimide (PI).[14] Under the appropriate conditions the addition of high-performance engineering thermoplastics led to phase separation into different phases.

On the other hand, attempts have been made to dissolve homogeneous thermoplastics in epoxy resins.[15–17] Using this technique implies the formation of a semi-interpenetrating polymer network (semi-IPN), which blends two polymers by entangling with their networks without the two networks chemically bonding with each other. The formation of a semi-IPN structure makes it possible to blend homogeneously the epoxy matrix and the thermoplastic or to disperse uniformly the thermoplastic in the epoxy matrix at a microscopic level. The semi-IPN network shows the combined properties of both polymers because of the composite structure at the molecular level.

Previously we reported about the synthesis and toughening effect on thermosets of PES–PEES [poly(ether ether sulfone)] copolymers with different reactive groups.[18–22] PES–PEES copolymers with amine end groups were blended with different epoxy resins, and their effects on thermomechanical[23] and rheological properties[24] were examined.

The objective of the present study was to investigate the effects on thermomechanical properties and morphology of an epoxy system based on diglycidyl ether of biphenol S (DGEBS) and 4,4′-diaminodiphenyl sulfone (4,4′-DDS) blended with PES–PEES, amine-ended copolymers.

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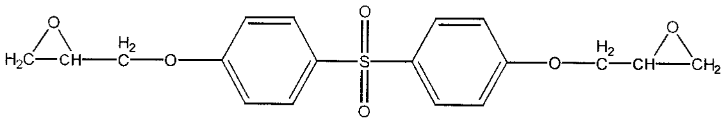
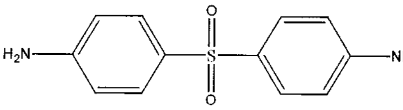
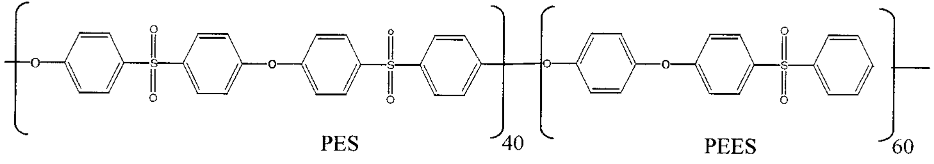


DGEBS



4.4’DDS



Five epoxy systems in which the amount of toughening agent was varied were fully characterized in morphology, viscoelastic properties, and fracture resistance. A single-phase morphology was observed for all the systems studied by transmission electron microscopy (TEM) analysis. The morphological observations were confirmed by dynamic thermal analysis (DMTA), which showed a single peak for all the analyzed samples because of a $T_g$ transition. An increase in $T_g$ values of the blend occurred from increasing the quantity of thermoplastics. The addition of a modifier also improved the toughness of the epoxy resin without having negative effects on tensile properties. The results of the analysis led us to the conclusion that a semi-interpenetrating network is formed as a result of the blending of the reactive copolymer, PES–PEES, within the DGEBS/DDS system.

## EXPERIMENTAL

### Materials and preparation of samples

The epoxy resin used in the experiments was a diglycidyl ether of biphenol S resin (Epiclon 830S) supplied by Shell, having epoxy equivalent weight of 181.04. The treating agent used was 4,4′-diaminodiphenyl sulfone supplied by Aldrich. The toughening agent used was an amine ended-copolymer, PES–PEES (40:60), prepared in our laboratories, with a molecular weight ($M_n$) of 12,000. The treating agent was added in a 77% stoichiometry ratio. Treated samples were prepared by mixing the thermoplastic and resins and by stirring the resulting mixture for 2 h at 120°C. Then the treating agent was added and the mixture stirred for 1 h at 80°C. After that the blended resin mixture was poured into a preheated silicone rubber mold and degassed for 30 min at 145°C. Then the temperature was increased at 2°C/min to 180°C and held at this temperature for 3 h. At the end of the treatment cycle the panels were left to cool down slowly at room temperature. The formulations of the systems studied are listed in Table I.

### Morphological analysis

Ultrathin sections of the modified epoxy resins were cut and examined using a transmission electron microscope (TEM; JEM-1200EX, JEOL Co. Ltd.) to observe the microstructure. Specimens for the TEM observations were stained with ruthenium tetroxide ($RuO_4$).

### Mechanical analysis

Molded plaques were used to produce samples for the following mechanical tests. A 3-point bend test was carried out at 5 mm/min using a sample size of 50 × 10 × 3 mm to measure the flexural modulus. The yield strength ($\sigma_y$) was measured in compression mode using a sample size of 10 × 10 × 3 mm. The crack opening stress intensity factor (*Kc*) was measured at 1 mm/min using a sample size of 70 × 10 × 3 mm with a single-edge notch. All measurements were made at 23°C.

### DMTA analysis

DMTA tests were carried out for treated samples by a dynamical mechanical thermal analyzer, MK IV, by Rheometric Scientific, at a fixed frequency of 1 Hz

**TABLE I**
**Formulations of the Systems Analyzed (% by Weight)**

| Component/system | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| EPICLON 830 | 79.11 | 75.16 | 67.25 | 59.33 | 55.38 |
| 4,4′ DDS | 20.89 | 19.84 | 17.75 | 15.67 | 14.62 |
| 40:60 PES/PEES | 0 | 5 | 15 | 25 | 30 |

with a 2°C/min heating rate using samples of sizes of 4.5 × 10 × 3 mm. Dynamic modulus and tan δ were obtained by a dual cantilever mode.

## RESULTS AND DISCUSSION

It is already well known that the mixture of epoxy resins and PES shows a lower critical solution temperature (LCST) phase diagram, as shown schematically in Figure 1. An increase in the molecular weight of an epoxy species gives rise to a decrease in the cloud point curve and therefore for a fixed fraction of PES to the demix of the thermoplastic phase. The morphology is frozen when the $T_g$ exceeds the treating temperature.

Consequently, the final morphology is the result of the competition between the molecular-weight increase of epoxy, leading to phase separation, and the simultaneous crosslinking, which suppresses phase separation.

The TEM analysis, summarized in Figure 2, showed no morphology for all the samples studied. According to the mechanism explained above, this would mean that the gelation of resin occurred before any phase-separation mechanism.

Nevertheless, we should note that the copolymer used in this study is characterized by a high chemical affinity between epoxy resin and the treating agent. All the reactants of the system are characterized by the presence of a sulfone group in their chains. Moreover, the presence of an amine group, as end group of a copolymer, is more likely to react with the epoxy group. In fact, as we have previously reported,[23] the copolymer acts as a treating agent for the epoxy resins.

In addition, what was observed by TEM could be related to the formation of an interpenetrating polymer network that would justify the homogeneous morphology.

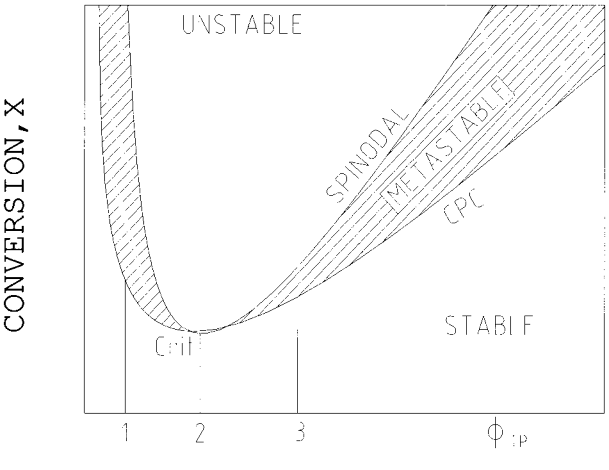
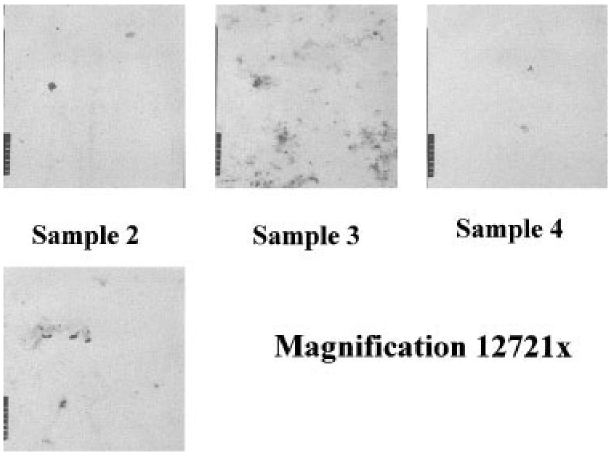


**Figure 1** Schematic phase diagram for a epoxy/PES blend.



**Sample 2** **Sample 3** **Sample 4**

**Sample 5**

**Magnification 12721x**

**Figure 2** TEM micrographs.

Other researchers have reported[15–17,25] about the formation of a semi-interpenetrating network characterized by an entanglement of the components without chemical bonding. In particular, the research by Mimura and colleagues[25] was based on the use of PES without reactive groups in the chains.

The formation of a semi-IPN structure makes it possible to blend homogeneously the epoxy matrix and thermoplastics or to disperse microscopically the thermoplastics in the epoxy matrix. The blend produced by a semi-IPN structure has the combined properties of both polymers because of the composite structure at the molecular level.

In our study the aforementioned chemical affinity between the epoxy, the treating agent, and the thermoplastics was found likely to improve the miscibility of the reactants, which would justify the absence of phase separation during the treating reaction. Moreover, the presence of reactive end groups in the copolymer chain gave rise to the formation of crosslink points that could act as permanent entanglement points.

The tan δ measurements, shown in Figure 3, provide further evidence of the absence of phase inversion. For all the formulations studied, a single peak was shown for systems with phase-inverted morphology that usually would show a double peak in correspondence with the $T_g$ values of both blended materials.

It is interesting to note he $T_g$ values of the blend significantly increased by increasing the amount of thermoplastics. In our previous studies[23] we showed that PES–PEES copolymer can act as a treating agent for epoxy resin. The observed effect on the $T_g$ of the epoxy phase can be related to the contribution of the low tail components of the PES–PEES copolymer that change the stoichiometry of the system. In fact, it is well known that an increase in treating-agent concen-

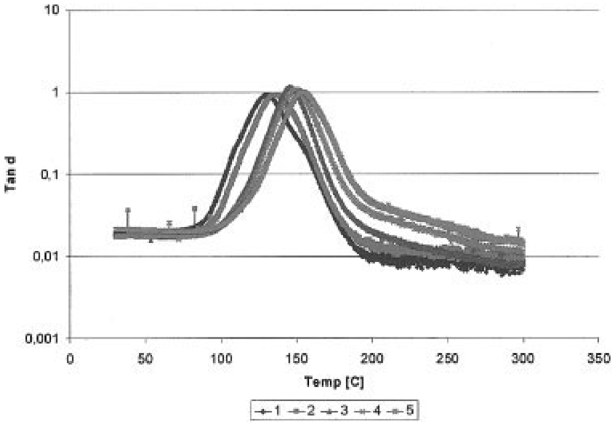


**Figure 3** Tan δ behavior of the samples studied.

tration enhances the crosslink density and leads to an increase in $T_g$.

The behavior of the elastic modulus, $E'$, can be seen in the graph in Figure 4, which shows an increase in the elastic modulus in the rubbery region for all the modified resin samples. This increase can be attributed to the formation of a semi-interpenetrating polymer network characterized by crosslink points, as previously mentioned. High moduli in the rubbery region also can be observed in the semi-IPN network characterized only by physical entanglement, obtained by the use of nonreactive PES.[25]

A high modulus in the rubber region is a positive feature resulting from using the semi-IPN technique. If a nonreactive copolymer had been used in the study, the system with phase-separated morphology would have shown a decrease in modulus in the rubbery region because of the transition of the copolymer from the glass to the molten state.

Mechanical tests were carried out on the treated samples to characterize the tensile and toughness properties of the resins, to which different amounts of thermoplastics had been added. The results are summarized in the graphics of Figure 5.

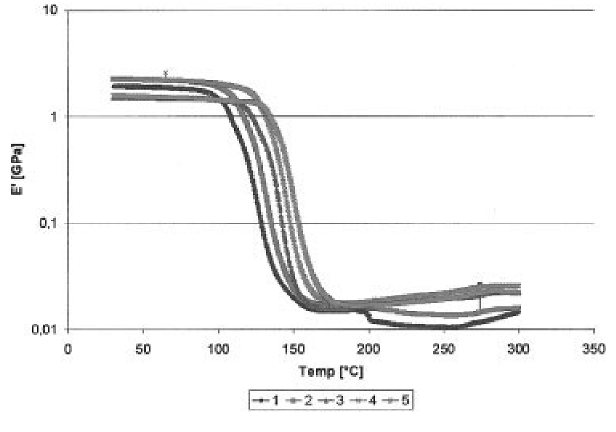


**Figure 4** Elastic modulus behavior of the samples studied.

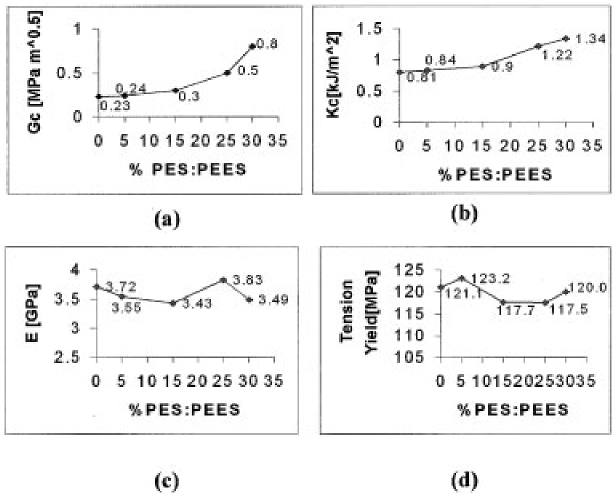


**Figure 5** Mechanical properties: (a) Energy of fracture versus thermoplastic content; (b) Stress intensity factor versus thermoplastic content; (c) Elastic modulus versus thermoplastic content; (d) Tension yield versus thermoplastic content.

The graphs in Figure 5(a,b) show the toughness measurements in terms of stress energy of fracture (*Gic*) and intensity factor (*Kc*). Both curves show an increase in toughness depending on an increase in the amount of thermoplastics. *Gic* values 3.5 and 2 times higher were observed for samples 5 and 4, respectively. No significant increases in toughness were obtained for samples 2 and 3.

It has been reported in the literature[25] that in toughened epoxies characterized by a phase-separated morphology, the progress of crack is prevented by dispersed particles of the thermoplastic component. The crack is split into some branches to avoid progressing through the dispersed particles. Accordingly, it may be concluded that the increase in toughness of the particulate resins is a result of depressing crack growth by the formation of branches.

This toughening mechanism cannot be applied to homogeneous systems, as in the mixtures of our study thermoplastics were finely dispersed within the resin matrix. When a homogeneous blend is obtained, the toughening mechanism is thought to be a pure deformation of the matrix.

Figure 5 shows the behavior of the elastic modulus [Fig. 5(c)] and of the yield strength in tension, $\sigma_y$ (7d), for blends containing various amounts of the copolymer PES–PEES. The elastic modulus and the $\sigma_y$ did change significantly when the thermoplastic was added. In our previous studies[23] we noticed a small decrease in elastic modulus with an increase in the amount of modifier, which was in accordance with results from other investigators[10,26]; however, it should be noted that in such cases the systems were characterized by phase-separated morphology.

Modifications[27] of the system studied by McGrath, whose aim was to improve the miscibility of the components, resulted in single-phase morphology with increases in the elastic modulus of the resulting mixtures. Consequently, we can say that the independence of the modulus and of $\sigma_y$ from the addition of thermoplastics can be attributed to the formation of a unique semi-IPN network.

## CONCLUSIONS

Fracture toughness measurements confirmed the remarkable effect of an amine-ended copolymer that can be used to increase the impact resistance of inherently brittle epoxy resins. No decrease in elastic modulus and strength yield in tension were found. TEM and viscoelastic analysis showed the presence of a single-phase morphology that can be attributed to the formation of a semi-IPN network. The addition of the novel PES–PEES copolymer resulted in a remarkable increase in the $T_g$ of the resulting network.

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