Curing and Toughening of a Styrene-Modified Epoxy Resin

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ABSTRACT: A commercially available epoxy resin (E907) formulated with a viscosity-reducing styrene monomer and several additives was subjected to thermal cure studies and mechanical property measurements. Thermoplastic poly(arylene ether sulfone) (PES) and poly(arylene ether phosphine oxide) (PEPO) with reactive amine or hydroxyl end groups were utilized to toughen and co-cure with the system. The cure cycle was optimized and the networks were analyzed via differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical analyzer, scanning electron microscopy, sol–gel extractions, and fracture toughness. A model epoxy resin was prepared from a tetrafunctional epoxy, e.g., MY722, difunctional EPON828, styrene monomer, and benzoyl peroxide initiator (BPO), and was evaluated as a control to assess the possible role of the styrene monomer. The optimized cure cycle for E907 was 6 h at 93°C, followed by a postcure of 2 h at 204°C. The fracture toughness of E907 was increased only marginally with PES and PEPO. In contrast, the model epoxy resin demonstrated a positive effect due to the styrene monomer and BPO and exhibited significantly increased fracture toughness with PES modification. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1504–1513, 2001

Key words: epoxy resin; styrene monomer; free radical initiator curing; reactive thermoplastic toughener; fracture toughness

INTRODUCTION

High performance composites and structural adhesives for aerospace applications have focused increased attention on epoxy resins due to their exceptional properties, including economics, excellent thermal and mechanical properties and solvent resistance. However, the low fracture toughness and high viscosity have prevented their wider use and have thus been the research topics for decades.[1]

Several studies have indicated that the fracture toughness of epoxy resins could be enhanced by the incorporation of functionalized rubber[2–4] or high performance thermoplastic polymers.[5–9] However, it has also been widely accepted that improved fracture toughness via rubber modification compromised thermal and mechanical properties,[4] while simple amorphous thermoplastic polymer blends reduced solvent resistance.

Reactive thermoplastic tougheners have proven to be ideal tougheners in improving not only fracture toughness,[10–15] but also adhesive properties[14,15] *without* sacrificing thermomechanical behavior and chemical resistance. The combination of high fracture toughness and

PES-NH$_2$

PEPO-NH$_2$
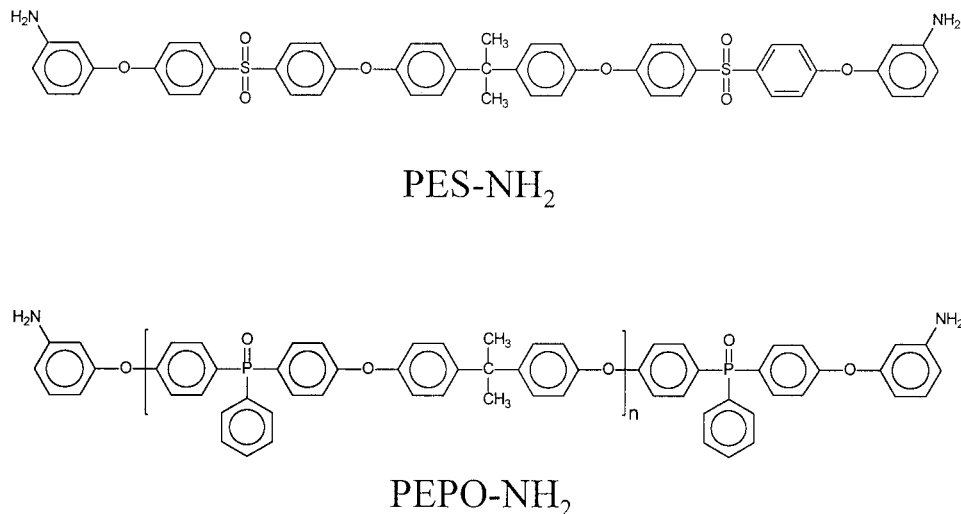
Figure 1 Chemical structure of poly(arylene ether)s.

good chemical resistance has been attributed to the chemical bond formation between the reactive groups of the toughener and the epoxy resins. Reactive thermoplastic poly(arylene ether)s have also been utilized for toughening bismalimides,[16,17] cyanate esters,[18] s well as epoxy resins.[19] In fact, ICI Fiberite commercialized reactive thermoplastic toughened epoxy resin prepreg with the trade name of E977.[20]

Processability is another important factor that should be considered since it also plays an important role in reducing manufacturing costs. The incorporation of styrene monomer into dimethacrylate or "vinyl ester" resins is one method for reducing melt viscosity and improving processability. Unfortunately, there are still many questions of how the styrene monomer copolymerizes during the cure and how this determines the final properties of the network.

This paper has investigated a new styrene-modified epoxy resin (E907) formulated by British Petroleum (BP) to facilitate injection moding. Fracture toughness and thermal properties were measured as a function of cure cycle and the reactive thermoplastic tougheners prepared in our laboratory. In an attempt to clarify the role of styrene monomer, a model epoxy resin was prepared from tetrafunctional (MY722) and difunctional systems (EPON828), and properties were evaluated as a function of the styrene content and free radical initiators such as benzoyl peroxide (BPO).
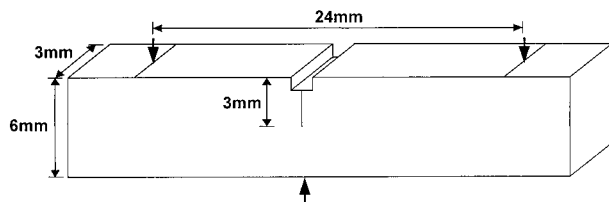
EXPERIMENTAL

Materials

The epoxy resin (E907 Part A), aromatic curing agent (Part B) and curing accelerator (Part C) were provided by BP. The E907 epoxy resin is known to contain multifunctional epoxy resins, a toughener, and viscosity reducer, which could be confirmed as styrene monomer, even by its characteristic odor. The E907 epoxy resin without the toughener (E907-NT) was also provided, but the toughener was not identified.

Reactive poly(arylene ether sulfone) (PES) with amine or hydroxyl end groups, and amine terminated poly(arylene ether phophine oxide) (PEPO) were prepared[14−16] and utilized as tougheners for E907 epoxy resins (Fig. 1). The molecular weight of thermoplastic tougheners was controlled to afford an M_n of 15,000 g/mole. The detailed synthesis of the poly(arylene ether)s is provided elsewhere.[12−15]

Cure Study of E907 Resin

The cure behavior of the E907 epoxy resin was monitored by differential scanning calorimetry (DSC). The E907 epoxy resin (78.7% Part A, 20.5% Part B, 0.8% Part C) was transferred into a 2.5×15 cm test tube and placed into a silicone oil bath. Initially, a one-step cure was attempted at 149°C (300°F), 121°C (250°F), 93°C (200°F), or at room temperature. The gelation and vitrification rates were measured by monitoring the cure re-

Figure 2 Schematic diagram of SENB sample.

action every 5, 10, 30, or 60 min, depending on the cure temperature. All experiments were done in a fume hood due to the odor of the styrene monomer.

A significant loss of styrene monomer was noted during the high temperature cure, which necessitated that a two-step cure be employed; i.e., 6 h at 93°C and additional 2 h at 149, 177, or 204°C. Cured samples were again analyzed by DSC to monitor the reaction and selected samples were subjected to dynamic mechanical analyzer (DMA) and thermogravimetric analysis (TGA) analysis. The extraction study was carried out in chloroform and tetrahydrofuran (THF) for 4 days via a Soxhlet Extractor to estimate the gel fraction.

E907 Epoxy Resin Toughening

E907 and E907-NT resins were toughened by either PES (hydroxyl or amine terminated) or PEPO (amine terminated). The concentration of the thermoplastic toughener was 7 wt % for E907, and 7 and 14 wt % for E907-NT. Toughening was carried out by dissolving the reactive thermoplastic in the epoxy resin at around 100°C, followed by the addition of the curing agent and accelerator. The mixture was then added to a silicone rubber mold, and cured in an air convection oven via the optimized cure cycle.

Property Measurements

The thermal behavior of the epoxy resins was determined by differential scanning calorimeter (TA DSC-2010) at a heating rate of 10°C/min. However, T_g of the samples such as toughened E907 epoxy resins were not be measured due to the high crosslinking density. Thus those samples were subjected to dynamic mechanical analysis (TA DMA-980) at 10°C/min and 1 Hz with a sample size of $3 \times 6 \times 30$ mm. The plane strain fracture toughness (K_{IC}) was measured with single-edge-notched bending (SENB) specimens, following ASTM Standard D-5045-91 (Fig. 2). The

cured samples were treated with emery paper to afford a rectangular shape ($3 \times 6 \times 40$ mm).

The specimens were then sawed to generate a notch and a crack was initiated by tapping with a fresh, liquid nitrogen chilled razor blade. The samples were tested in a 3-point bending mode at the test rate of 12.5 mm/min. Approximately 10 samples were tested and fracture toughness values were calculated by the formula provided in ASTM D-5045-91. The phase separation behavior of cured samples was also investigated with scanning electron microscope (SEM, JEOL JSE-5800). All samples were coated with Au-Pd to avoid charging and head build-up problems.

Model Study

A model epoxy resin was prepared and evaluated to assist in understanding the chemical interaction of the styrene monomers in the E907 epoxy resin. A model epoxy resin was prepared from MY722 (a tetrafunctional epoxy resin from Ciba-Geigy) and EPON828 (a difunctional epoxy resin from Shell). The mixing ratio was 25 wt % for the MY722 and 75 wt % for the EPON828, which was designed to give a T_g of approximately 200°C, similar to that obtained from the E907. The model epoxy resin was cured at 93°C for 6 h, followed by 2 h at 204°C with and without the styrene monomer (10 phr), BPO (0.1 phr) and/or PES-NH$_2$ (14 or 20 wt %). Thermal properties and fracture toughness were evaluated as previously described. Although the exact structure of the aromatic curing agent Part B was not identified, it was used as a curing agent for the model epoxy resin in order to compare it with the E907.

RESULTS AND DISCUSSION

Cure Cycle Optimization for E907 Epoxy Resins

E907 epoxy resins cured in an oil bath at 149°C (300°F), 121°C (250°F), 93°C (200°F), or at room

Table I Time for Vitrification and Gelation of E907

Cure Temp. (°C)	Time$_{gel}$	Time$_{vit}$	
RT	3 days	4–6 days	
93	3 h	4–5 days	
121	40 min	65 min	Bubbling
149	15 min	20 min	Vigorous bubbling

Table II T_g **of E907 as a Function of Cure Cycle**

Cure Cycle	T_g (°C)	
	1st Scan	2nd Scan
RT/6 days	Exo	197
93°C/6 h	Exo	190
121°C/1 h	Exo	190
149°C/20 min	Exo	182
93°C/6 h + 149°C/2 h	—	180
93°C/6 h + 177°C/2 h	175	184
93°C/6 h + 204°C/2 h	183	200

Figure 3 TGA of E907 cured at RT, 93, 121, and 149°C.

temperature took 15 min, 40 min, 3 h, and 3 days, respectively to reach the gelation stage (Table I). Curing at 121 and 149°C generated bubbles, which were particularly severe at the higher temperature, and likely attributable to evaporation of styrene monomer. Therefore, it was suggested that the E907 resin be cured at 93°C to avoid both premature boiling of styrene monomer. However, since it was not possible to achieve a fully cured epoxy resin at this temperature, a two step-cure was followed.

In the two-step cure, the E907 epoxy resins were first cured for 6 h at 93°C, followed by additional 2 h at 149, 177, or 204°C. The samples cured at 93–149°C showed an exothermic peak in the first scan (Table II) and a T_g of 180°C. On the other hand, the two-step cure (93–177°C and 93–204°C) resulted in T_gs of 183 and 200°C in the first and second scan, respectively, indicating a fully cured system.

The TGA thermograms of the E907 cured at room temperature (RT) or at 93°C displayed significant weight loss, starting at approximately 100°C, probably due to the styrene monomer or oligomer (Fig. 3). However, the loss was relatively minor for the samples cured at 121 or 149°C, which could be explained by the slow evaporation of styrene monomer relative to the polymerization of styrene monomer during the cure.

The degree of cure was measured via the gel fraction, based on extraction studies in CHCl$_3$ and THF. As indicated in Table III, the samples cured at 93 and 93–149°C showed 25 and 11% loss, respectively, which is indicative of a partial cure. However, the cure cycles of 93–177 and 93–204°C provided 1–2% loss, indicating fully cured samples, which can also be verified by subsequent TGA results. Although the 93–177°C cure may

have been sufficient, 93–204°C was employed since the cured E907 showed a T_g of 200°C.

Property Measurements of E907 Epoxy Resin Networks

The cured E907 and E907-NT epoxy reins exhibited T_gs of 216 and 226°C, respectively, which were measured from the tan δ of DMA (Fig. 4). The T_g difference may have resulted from the influence of the toughener utilized by BP. The E907 epoxy resin exhibited two T_gs (220 and 182°C) when toughened with PES-OH (7 wt %); but a single T_g at 202 or 224°C when PES-NH$_2$ or PEPO-NH$_2$ was utilized (Table IV), respectively. However, all the toughened E907-NT with 7 and 14 % PES or PEPO demonstrated two T_gs (Table IV). With regard to the 14% sample, the upper T_g at around 220°C is thought to correspond to the E907-NT epoxy part, while the lower T_g at around 180°C approximates the T_g of PES or PEPO. However, the sample with 7% PES or PEPO demonstrated T_g at approximately 150°C, which was lower than that of PES or PEPO. This could be attributed to the polymerized styrene monomers

Table III   Solvent Extraction Results of Cured E907

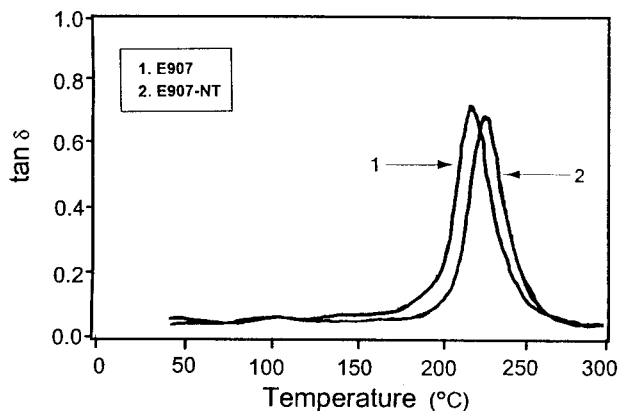| Cure Cycle	Weight Extracted (%)	
	CHCl$_3$	THF
93°C/6 h	25	25
93°C/6 h + 149°C/2 h	11	10
93°C/6 h + 177°C/2 h	2	3
93°C/6 h + 204°C/2 h	1	4

Figure 4   DMA of E907 and E907-NT.

in E907-NT; the T_g of 150°C is from the mixture of PES and PS. The E907 toughened with 7% PES-OH showed a similar T_g, as did the E907-NT with 14% PES-OH, which can be explained by the incorporation of the toughener to the E907.

The fracture toughness of the E907 was 0.53 MPa-m$^{0.5}$ and marginally increased with 7 wt % PES-NH$_2$ (0.59) and PES-OH (0.63) (Table V). However, relatively low fracture toughness (0.40 MPa-m$^{0.5}$) was observed for the E907-NT, which was comparable with 0.3 MPa-m$^{0.5}$ with MY 721 epoxy resin,[14,15] indicating the effect of BP's thermoplastic toughener. When PES or PEPO was added, the fracture toughness of the E907-NT increased to the order of 0.5 MPa-m$^{0.5}$ with 7 wt % and 0.6 MPa-m$^{0.5}$ with 14 wt % concentrations. The fracture toughness of the E907 with 7% PES-NH$_2$ was similar to the E907-NT with 14% PES-NH$_2$, but slightly higher than that of the E907-NT with 7% PES-NH$_2$. This mirrors the T_g changes shown in Table IV, and thus could be attributed to 5 wt % thermoplastic toughener added to the E907 by BP.

Phase Separation Behavior of E907 Epoxy Resins

The SEM micrographs of cured E907-NT (no thermoplastic toughener) exhibited a clean fracture surface with an aggregate of 1 μm spheres [Fig. 5(A)]. Therefore, it is hypothesized that this aggregate was formed from the styrene, which polymerized during the cure. At 7% concentration of PES-NH2, PES-OH, and PEPO-NH$_2$, the E907-NT showed a second phase 1–2 μm in size, which in turn was an aggregate of small spheres [Fig. 5(B)]. The number of second phase particles decreased in the order of PES-OH, PES-NH$_2$, and PEPO-NH$_2$.

The E907-NT formed co-continuous morphology at 14% of PES-OH, PES-NH$_2$, and PEPO-NH$_2$ [Fig. 5(C, D)]. In the toughener/styrene continuous phase, an unusual morphology was observed. PES-OH toughened samples showed a large gap between the sphere and the continuous phase, which hypothetically provides good adhesion between them due to the OH groups in the PES. In the PES-NH$_2$ or PEPO-NH$_2$ toughened samples, the spheres in the toughener/styrene continuous phase showed a large size distribution and good adhesion to the toughener/styrene layer, but no breakage of spheres. This unusual morphology could be attributed partially, if not wholly, to the presence of the styrene, which polymerized during the cure.

The cured E907 resin, containing the toughener and a styrene monomer, also showed a small second phase (0.5 μm) as well as aggregates (3–5 μm) [Fig. 6(A)]. The E907 epoxy resin toughened with 7% of PES-NH$_2$, and PEPO-NH$_2$ showed similar phase separation behavior [Fig. 6(B)]. As expected from the T_g results, the PES-OH toughened E907 epoxy resin showed much better phase separation behavior than PES-NH$_2$ or PEPO-NH$_2$ toughened samples [Fig. 6(C)]. The different phase separation behavior of the E907 and E907-NT materials could have resulted from the BP thermoplastic toughener, which may have a different chemical structure, molecular weight and/or end groups from the toughener utilized in this study.

Model Study with MY722 and EPON828

The model epoxy resins prepared from MY722 (75 wt %) and EPON828 (25 wt %) were cured with aromatic curing agent Part B supplied by BP with or without PES-NH$_2$, styrene monomer (10 phr) and/or BPO (0.1 phr). A T_g of 204°C was obtained by DSC from the MY722/EPON828 mixture (Table VI), which approximates that of the E907

Table IV T_g of Toughened E907 and E907-NT by DMA

	E907, 7 wt %	E907-NT	
		7 wt %	14 wt %
Cont.	216	226	226
PES-NH$_2$	202	152, 218	176, 220
PES-OH	182, 220	152, 221	178, 228
PEPO-NH$_2$	224	152, 221	180, 222

Table V K_{IC} Fracture Toughness of E907 and E907-NT

| Toughener	K_{IC} Fracture Toughness		
	E907, 7 wt %	E907-NT	
		7 wt %	14 wt %
Cont.	0.53 ± 0.02	0.40 ± 0.13	—
PES-NH$_2$	0.59 ± 0.05	0.52 ± 0.08	0.61 ± 0.05
PES-OH	0.63 ± 0.13	0.50 ± 0.08	0.65 ± 0.11
PEPO-NH$_2$	—	0.56 ± 0.09	0.64 ± 0.12

shown in Table II. The resin mixture with 14 wt % PES-NH$_2$ showed two T_gs when styrene or styrene/BPO was added. However, when 20 wt % PES was utilized, two T_gs were observed in all samples.

K_{IC} fracture toughness of the control sample (75% EPON828+25% MY722) was 0.38 MPa-m$^{0.5}$ and increased to 0.69 (14 wt % PES), 0.73 (14 wt % PES + 10 wt % styrene), and 0.72 MPa- m$^{0.5}$ (14 wt % PES + 10 wt % styrene + BPO). These values are comparable to the fracture toughness of the E907-NT with 14 wt % PES or PEPO. It should be noted that the addition of the styrene monomer and/or BPO did not appreciably increase the fracture toughness of the epoxy resin. However, the epoxy resin with 20 wt % PES-NH$_2$ exhibited fracture toughness of 1.05 MPa-m$^{0.5}$, which is much higher than that obtained with 14 wt % PES-NH$_2$ (Table VII). Moreover, the fracture toughness increased dramatically when

(A)

(B)

(C)

(D)
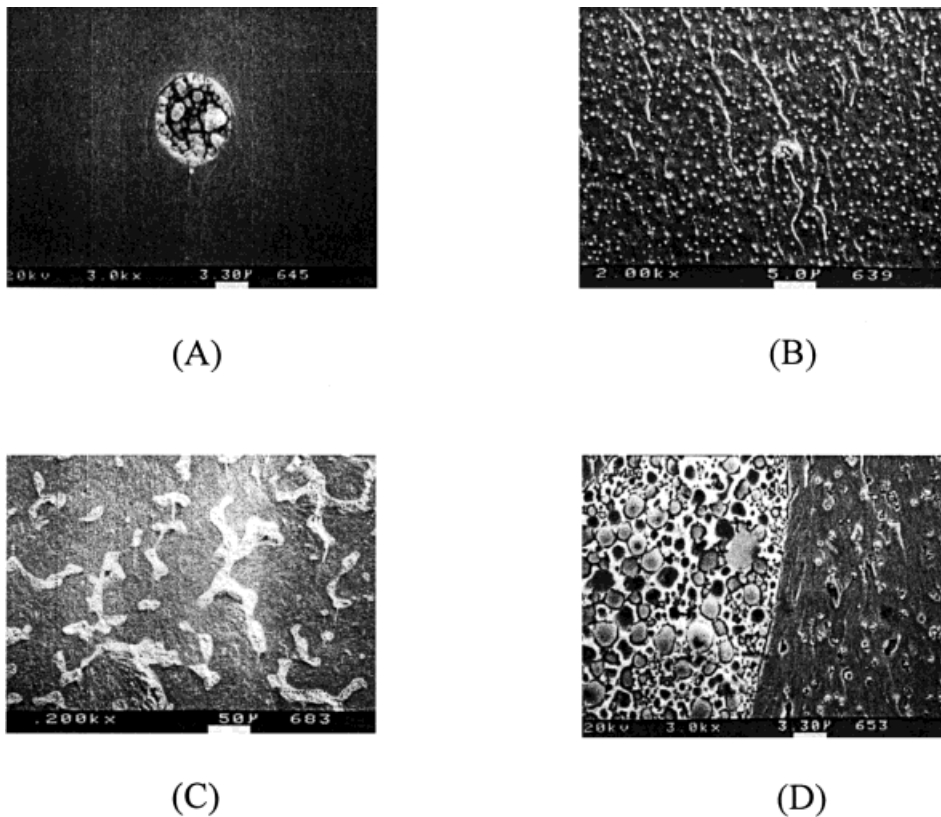
Figure 5 SEM micrographs of PES toughened E907-NT epoxy resin. A: E907-NT; B: E907-NT+ 7 wt % PES-NH$_2$; C: E907-NT+ 14 wt % PES-NH$_2$; D: PES-OH 7 wt %.
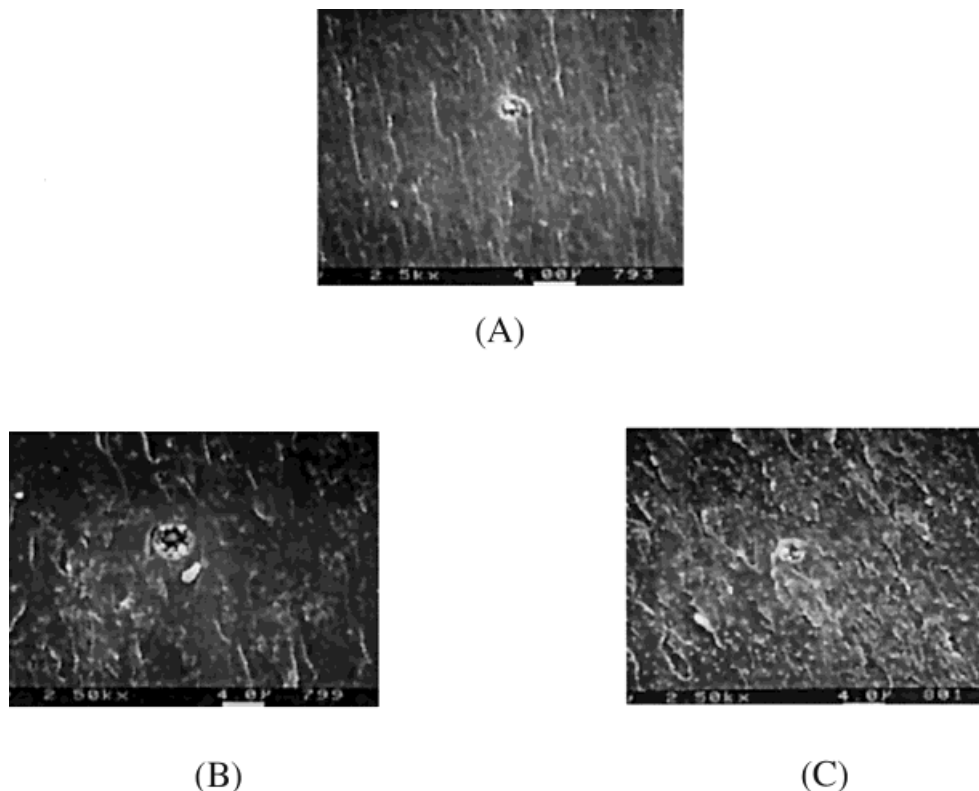
Figure 6 SEM micrographs of PES toughened E907 epoxy resin. A: E907; B: E907+ 7 wt % PES-NH$_2$; C: E907+ 7 wt % PES-OH.

PES/styrene (1.22 MPa-m$^{o.5}$) or PES/styrene/BOP (1.65 MPa-m$^{o.5}$) were added, which could be explained by better phase separation behavior with styrene and/or BPO as evidenced by SEM analysis.

As observed from the SEM micrographs, the EPON828+MY722 samples with 14 wt % PES-NH$_2$ showed a dispersed second phase of approximately 1 μm in size (Fig. 7). This morphology is similar to that of the E907, as well as the E907-NT with 7 wt % PES-NH$_2$— except for the aggregation of spheres. The size of the second phase increased and the edge of the particle ap-

pears deeper as styrene and styrene+BPO were added.

A co-continuous morphology was obtained with 20 wt % PES-NH$_2$ and the PES phase increased as styrene or styrene/BPO was added, indicating that the styrene had some effect on the phase separation behavior (Fig. 8). It was noted that epoxy spheres in PES continuous phase were broken in half when PES-NH$_2$ was utilized, indicating excellent adhesion between epoxy spheres and the PES phase. However, the samples containing styrene monomer and/or BPO exhibited rather ductile fracture of PES/styrene phase than bro-

Table VI T_g **Values of Model Epoxy Resin by DSC**

Epoxy Sample	14 wt %	20 wt %
E828 + MY722 (75/25)	—, 204	—
+PES	—, 201	180, 202
+PES + Styrene	173, 198	177, 198
+PES + St + BPO	174, 193	177, 200

Table VII K_{IC} **Fracture Toughness of Neat and Toughened Model Epoxy Resin**

Epoxy Sample	14 wt %	20 wt %
E828 + MY722 (75/25)	0.38 ± 0.09	
+PES	0.69 ± 0.05	1.05 ± 0.11
+PES + Styrene	0.73 ± 0.06	1.21 ± 0.20
+PES + ST + BPO	0.72 ± 0.02	1.65 ± 0.21

(A)

(B)

(C)

(D)
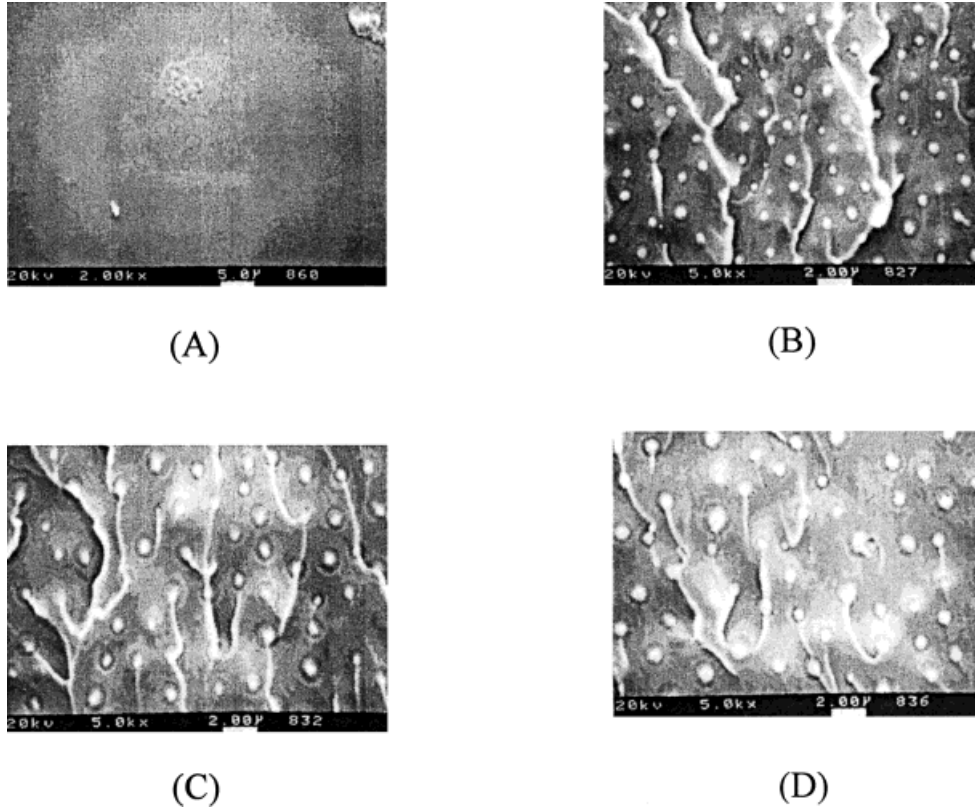
Figure 7 SEM micrographs of model epoxy resin from MY722 and EPON828. A: Model epoxy resin; B: with 14% PES-NH$_2$; C: with 14% PES-NH$_2$+styrene; D: with 14% PES-NH$_2$+styrene+BPO.

ken epoxy spheres [Fig. 8(B)]. The phase separation was even more noticeable when the free radical initiator BPO was used. It is believed that the styrene monomer, which was added polymerized during the cure, thus enhanced phase separation of PES. Ductile nature of PES/polystyrene, possibly due to a relatively low degree of polymerization of styrene, provided ductile fracture of PES/styrene instead of fracture of epoxy spheres, leading to improved fracture toughness of the model epoxy resin.

CONCLUSIONS

Commercial epoxy resins formulated by BP based on multifunctional epoxy resins, thermoplastic tougheners, and viscosity reducer were evaluated via thermal analysis, cure studies, and mechanical property measurements.

1. The optimized two-stage cure cycle for the commercialized E907 epoxy resin was 93°C/6h–204°C/2h, which avoided the loss of the viscosity reducing styrene at the higher temperatures.

2. The fracture toughness of the E907 and the E907-NT was only marginally increased with the addition of PES and PEPO.

3. The E907 exhibited only a second phase, which were particle aggregates. However, highly dispersed particles were observed with the E907-NT containing 7 wt % PES or PEPO, which is similar to that of the E907 with 7 wt % PES or PEPO. Co-continuous morphology was obtained with 14 wt % toughener.

4. The model epoxy resin (75%MY722+ 25%EPON828) showed marginally improved fracture toughness with 14 wt % PES, but greatly improved values at 20 wt % PES, which was even greater when styrene monomer and BPO were included, unlike the E907.

5. A dispersed morphology of PES was observed at 14 wt % PES, while co-continuous
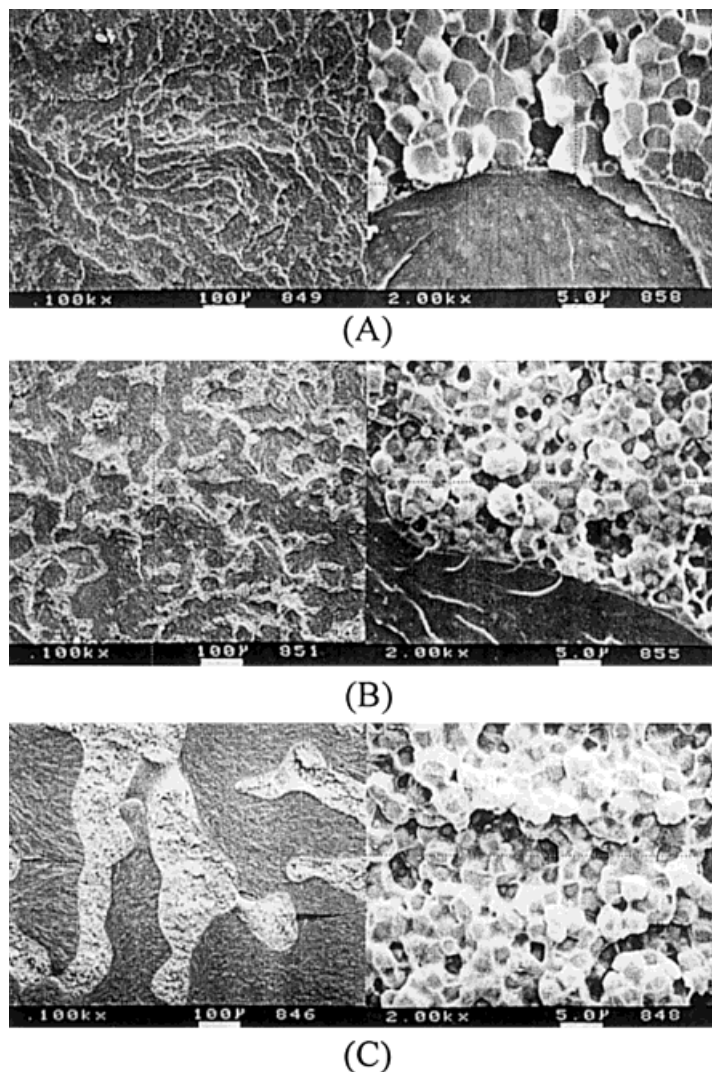
Figure 8   SEM micrographs of model epoxy resin from MY722 and EPON828. A: With 20% PES-NH$_2$; B: with 20% PES-NH$_2$+styrene; C: with 20% PES-NH$_2$+styrene+BPO.

morphology was observed at 20 wt % PES. Enhanced phase separation with styrene and/or BPO, and ductile failure of PES/polystyrene phase could be responsible for the improved fracture toughness of the model epoxy resin.

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