

Enhanced Fracture Toughness of Epoxy Resins with Novel Amine-Terminated Poly(arylene ether sulfone)–Carboxylic-Terminated Butadiene-Acrylonitrile–Poly(arylene ether sulfone) Triblock Copolymers

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ABSTRACT: Amine-terminated poly(arylene ether sulfone)–carboxylic-terminated butadiene-acrylonitrile–poly(arylene ether sulfone) (PES-CTBN-PES) triblock copolymers with controlled molecular weights of 15,000 (15K) or 20,000 (20K) g/mol were synthesized from amine-terminated PES oligomer and commercial CTBN rubber (CTBN 1300x13). The copolymers were utilized to modify a diglycidyl ether of bisphenol A epoxy resin by varying the loading from 5 to 40 wt %. The epoxy resins were cured with 4,4'-diaminodiphenylsulfone and subjected to tests for thermal properties, plane strain fracture toughness (K_{IC}), flexural properties, and solvent resistance measurements. The fracture surfaces were analyzed with SEM to elucidate the toughening mechanism. The properties of copolymer-toughened epoxy resins were compared to those of samples modified by PES/CTBN blends, PES oligomer, or CTBN. The PES-CTBN-PES copolymer (20K) showed a K_{IC} of 2.33 MPa m^{0.5} at 40 wt % loading while maintaining good flexural properties and chemical resistance. However, the epoxy resin modified with a CTBN/8K PES blend (2:1) exhibited lower K_{IC} (1.82 MPa m^{0.5}), lower flexural properties, and poorer thermal properties and solvent resistance compared to the 20K PES-CTBN-PES copolymer-toughened samples. The high fracture toughness with the PES-CTBN-PES copolymer is believed to be due to the ductile fracture of the continuous PES-rich phases, as well as the cavitation of the rubber-rich phases. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1556–1565, 2002; DOI 10.1002/app.10390

Key words: epoxy resin; poly(arylene ether sulfone)–carboxylic-terminated butadiene-acrylonitrile–poly(arylene ether sulfone) copolymers; fracture toughness

INTRODUCTION

Epoxy resins have been utilized in high-performance composite applications because of their

good thermal, mechanical, and adhesive properties; excellent solvent resistance; and high dimensional stability. However, a major drawback of epoxy resins is their inherent brittleness, which has led to extensive research efforts to improve their low toughness. A number of articles have reported that the fracture toughness of epoxy resins could be enhanced by the incorporation of functionalized rubbers,^{1–7} rigid particulate inor-

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ganic fillers,^{8,9} and high-performance thermoplastics such as poly(arylene ether sulfone) (PES) and poly(ether imide).^{10–15} Unfortunately, rubber incorporation detracts from the good thermomechanical properties of epoxy resins and leads to poor thermal stability and a low glass-transition temperature (T_g). On the other hand, commercial thermoplastic polymer blending results in poor solvent resistance and poor processability because of the absence of chemical bonds and the high molecular weight of the thermoplastic toughener, respectively.

However, the utilization of amine-terminated PES^{16–18} improved not only the fracture toughness but also the adhesive properties without sacrificing the chemical resistance, although the processability still remained relatively poor. Core-shell particles, which had a rubbery core and a hard polymer shell, were also introduced to toughen the epoxy resin and led to highly enhanced fracture toughness.^{19–23} However, there was a problem of uniform dispersion in the epoxy matrix unless loading was very high. Another approach was the utilization of rigid–rigid or rigid–soft polymers through blending,^{24–27} which had some synergistic effects. Unfortunately, this method also had drawbacks such as poor solvent resistance due to the absence of chemical bonds, limited solubility of the rigid polymer in the epoxy resin, and poor thermomechanical properties from soft polymers.

Therefore, in this study PES–carboxylic-terminated butadiene-acrylonitrile–PES (PES-CTBN-PES) triblock copolymers were synthesized from amine-terminated PES oligomers and commercial CTBN in order to improve the fracture toughness of epoxy resins without sacrificing the solvent resistance, processability, and thermomechanical properties. The toughened epoxy resins were evaluated by measuring their thermal properties, solvent resistance, plane strain fracture toughness (K_{IC}), and flexural properties. An SEM analysis was also carried out to elucidate the toughening mechanism. The properties of copolymer-toughened epoxy resins were compared to those samples modified by PES oligomer, CTBN, or PES/CTBN blends.

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol A (DGEBA) epoxy resin (Epikote 828, epoxy equivalent weight

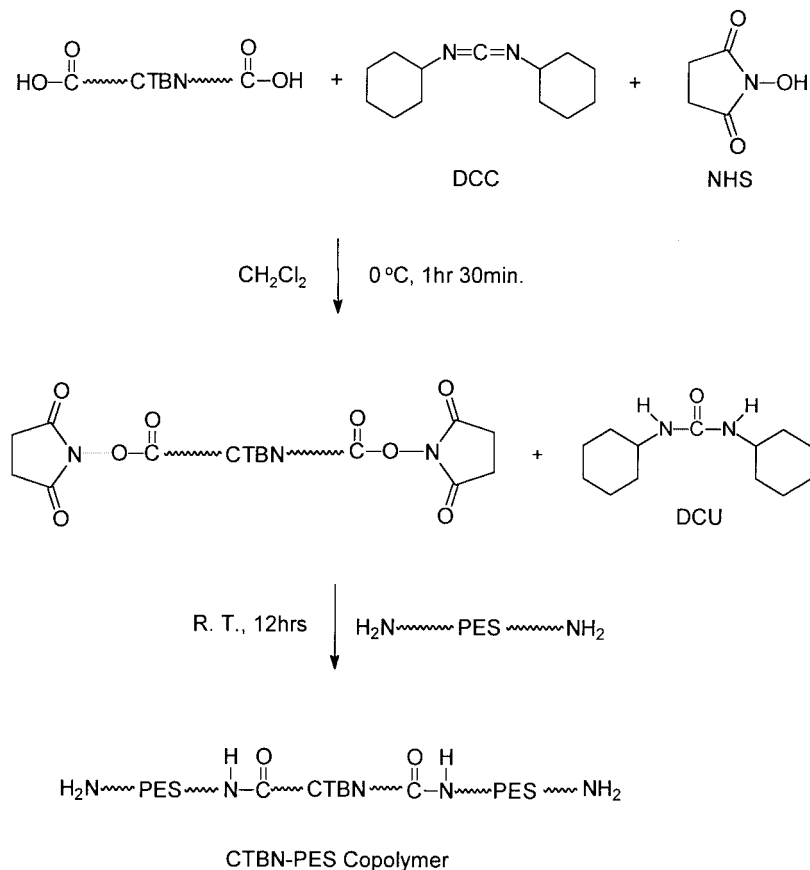
= 188) was kindly provided by Kumho-Shell and the curing agent 4,4'-diaminodiphenylsulfone (*p*-DDS) was purchased from Aldrich. Amine-terminated PES oligomers with molecular weights of 5,929 (6K) and 8,832 (8K) g/mol were prepared as previously reported¹⁷ and utilized to synthesize PES-CTBN-PES triblock copolymers with commercial CTBN rubber (CTBN 1300x13). For the synthesis of the copolymers, dicyclohexyl dicarbodiimide (DCC, Aldrich), *n*-hydroxysuccinimide (NHS, Aldrich), and methylene chloride (Fisher) were utilized after distillation

Synthesis and Characterization of PES-CTBN-PES Copolymers

Amine-terminated PES-CTBN-PES triblock copolymers prepared from CTBN 1300x13 and PES-NH₂ oligomers (6K and 8K) were controlled to have number-average molecular weights of 15,000 or 20,000 g/mol (15K and 20K, Scheme 1). Amine-terminated PES oligomers were prepared from dichlorodiphenylsulfone and bisphenol A via a nucleophilic aromatic substitution reaction.¹⁷ The copolymers were synthesized in a three-necked round-bottom flask equipped with a magnetic stirrer, a gas inlet, and a thermometer. The 15K PES-CTBN-PES triblock copolymer from 6K PES-NH₂ and CTBN 1300x13 was prepared as follows: 0.0031 mol (10 g) of CTBN and 300 mL of CH₂Cl₂ were charged into a flame-dried flask and stirred under nitrogen flow to obtain a clear solution, followed by the addition of DCC (2.5788 g, 0.0125 mol) and NHS (2.8775 g, 0.025 mol) to activate the carboxylic groups of CTBN.²⁸ The reaction mixture was then cooled to 0°C with an ice-water bath and allowed to react for 90 min to activate the carboxylic groups in CTBN by DCC and NHS. Then 37.056 g (0.063 mol) of 6K PES-NH₂ was charged into the reactor and allowed to react for 12 h at room temperature at 15% (w/v) solid concentration.

Once the reaction was completed, the polymer solution was diluted with CH₂Cl₂ and filtered to remove the by-products, *N,N*-dicyclohexylurea, and any remaining DCC and NHS. The polymer solution was then precipitated using a methanol/water (3:1) mixture, which was followed by filtering and drying. The powdery polymer was redissolved in chloroform and then precipitated into a methanol/water (3:1) mixture and filtered. The end product was dried overnight at room temperature and for an additional 12 h at 80°C.

The T_g values of the polymers were measured by DSC (TA-2010) at a heating rate of 10°C/min,



Scheme 1 Synthesis of amine terminated PES-CTBN-PES triblock copolymers.

and their thermal stabilities were determined by TGA (TA-2050) in air. The copolymer structure was analyzed by FTIR (Perkin-Elmer 2000). The end-group titration was carried out with an autotitrator (Metrohm 670), and GPC (Waters M77251 and M510) was also performed. The intrinsic viscosities were measured in chloroform at 25°C using a Canon Ubbelohde viscometer.

Toughening and Property Measurements of Epoxy Resins

The epoxy control samples were prepared by dissolving the curing agent (*p*-DDS) into the epoxy resin at 130°C, which was followed by curing at 130°C for 5 h and at 220°C for an additional 2 h. However, for the thermoplastic modifier it was first dissolved at 130°C without utilizing any solvent. After degassing in a vacuum oven, the curing agent DDS was dissolved in the epoxy resin, followed by another degassing step. The resin mixture was then poured into a preheated RTV silicon rubber mold and cured at 130°C for 5 h and

then at 220°C for an additional 2 h. The cured epoxy resin was slowly cooled to room temperature in an oven and subjected to property measurements. A 1:1 stoichiometry between the epoxy groups and the amine groups in the curing agent and modifier was maintained in order to maximize the properties.

The T_g of the cured epoxy resin was determined by DMA (TA-983) with a $3 \times 10 \times 60$ mm specimen at a heating rate of 10°C/min in resonance mode. TGA (TA-2050) was utilized at 10°C/min in air to measure thermal stability. The solvent resistance of these toughened epoxy samples was evaluated by immersing them ($3 \times 6 \times 20$ mm) in chloroform and monitoring the color and shape for 3 days at room temperature. The flexural strength and modulus were also measured according to ASTM D 790M-86 by using a 3-point bending test with an Instron 5567 at a cross-head speed of 1.0 mm/min and rectangular $3 \times 10 \times 60$ mm samples. Five or more samples were tested and the results were averaged.

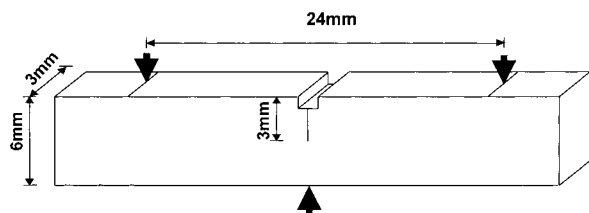


Figure 1 Schematic diagram of SENB sample.

The K_{IC} was measured with single edge notched bending specimens following ASTM D 5045-91 standard (Fig. 1). The specimens were ground with sandpaper to afford a smooth rectangular shape ($3 \times 6 \times 40$ mm). After making a notch at the center of the sample with a reciprocating saw, a sharp crack was initiated by tapping it with a liquid nitrogen chilled razor blade. Care was taken to ensure that the crack propagated about halfway through the specimen. The samples were tested in 3-point bending mode with an Instron 5567 at a cross-head speed of 12.5 mm/min. Approximately 10 samples were tested and their fracture surfaces were analyzed with SEM (Jeol JSM-5600) at 10 kV to investigate the phase separation behavior.

RESULTS AND DISCUSSION

Characteristics of PES-CTBN-PES Triblock Copolymers

The PES-CTBN-PES triblock copolymers prepared from PES and CTBN were characterized by DSC, TGA, GPC, FTIR, end-group titration, and viscosity measurements. In the FTIR analysis (Fig. 2) the C=O bands of the carboxylic group in CTBN (1712 cm^{-1}) shifted to 1690 cm^{-1} , indicating the formation of amide carbonyl stretching bands that resulted from the copolymerization. The copolymerization was also evidenced by the weakening of the C=C bands of CTBN at 1636 cm^{-1} and the N-H vibration of PES at 3381 cm^{-1} , as well as by the disappearance of the OH peak above 3150 cm^{-1} . As expected, the 15K copolymer exhibited stronger amide bands than the 20K copolymer, possibly because of the higher number of amide bonds in the 15K copolymer.

The molecular weights of the PES-CTBN-PES copolymers as determined by end-group titration were 16,072 and 19,628 g/mol, which correlated well to the target molecular weights of 15,000 and 20,000 g/mol, respectively (Table I). The intrinsic

viscosities of the 15K and 20K PES-CTBN-PES copolymers were 0.18 and 0.20 dL/g in *N*-methyl-2-pyrrolidinone, respectively. The relatively low intrinsic viscosities of the 15K and 20K PES-CTBN-PES copolymers, compared to the 6K PES (0.15 dL/g) and 8K PES-NH₂ (0.17 dL/g), could be explained by the very high chain flexibility of the CTBN unit in the copolymer. The GPC analysis of the PES-CTBN-PES copolymer revealed a sharp single peak, as did those of CTBN and PES (Fig. 3). However, the copolymer peak appeared earlier than CTBN and PES, indicating that the copolymer molecular weight was higher than that of CTBN and PES, and the copolymerization was successful. The molecular weights of the 15K and 20K PES-CTBN-PES copolymers measured by GPC were 14,967 and 21,820 g/mol, respectively, which matched well to the target molecular weights, as well as the titrated molecular weights.

As expected, the T_g values of the 15K PES-CTBN-PES copolymers were -26 and 160°C (Table I) whereas those of the 20K PES-CTBN-PES copolymers were -23 and 170°C . The lower T_g values are most likely from the CTBN rubber, and the higher ones correspond to the PES domain. It is noted that the T_g values of the CTBN domain were slightly higher than that of pure CTBN (-36°C), and the T_g values of the PES domain were a little lower than those of PES (167°C for 6K and 174°C for 8K; Table I). This may have resulted from slight phase mixing. As shown in Figure 4, the thermal stability measured by TGA in air indicated that the 20K PES-

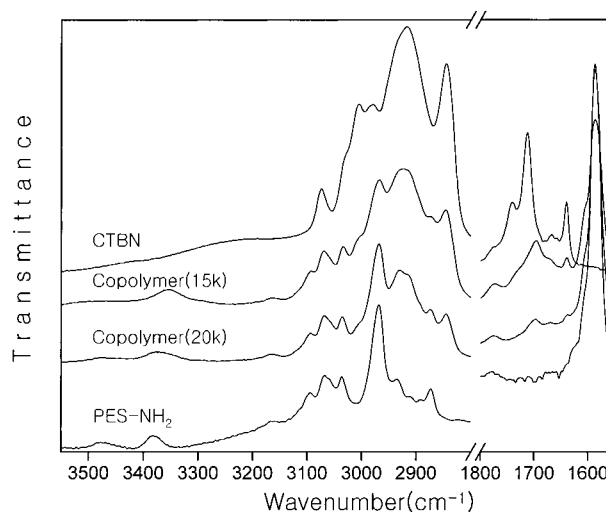


Figure 2 FT-IR of PES-CTBN-PES Copolymers.

Table I Characteristics of Tougheners for Epoxy Resin

	Target M_n	End Group	Titred ^a M_n	$[\eta]^b$ (dL/g)	T_g^c (°C)	T_d^d (°C)
PES-CTBN 13-PES (15K)	15,000	NH ₂	16,072	0.18	-26,160	398
PES-CTBN 13-PES (20K)	20,000	NH ₂	19,628	0.20	-23,170	417
PES-NH ₂ (6K)	5,500	NH ₂	5,929	0.15	167	447
PES-NH ₂ (8K)	8,000	NH ₂	8,822	0.17	174	481
CTBN: 1300 × 13	—	COOH	3,200	—	-36	330

^a Performed with an autotitrator (Metrohm).

^b The intrinsic viscosity $[\eta]$ at 25°C in CHCl₃.

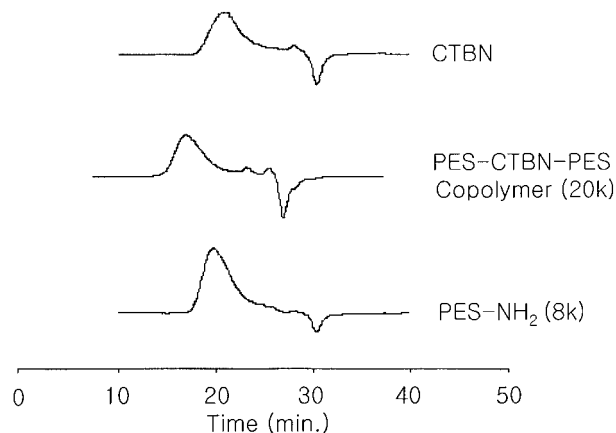
^c The glass-transition temperature (T_g) as found by DSC with a second heating in N₂.

^d The decomposition temperature (T_d) as found by TGA with a 5 wt % loss in air.

CTBN-PES copolymers have much better thermal stability than CTBN but they are slightly inferior to PES-NH₂(8K), as expected from the poor stability of CTBN.

Thermal Behavior of Toughened Epoxy Samples

The T_g value of the epoxy control samples was 223°C by DMA and it decreased with increased toughener incorporation, but the 20K PES-CTBN-PES copolymer-toughened epoxy samples provided T_g values of -9 and 218, -12 and 217, and -15 and 208°C at 10, 20, and 30 wt % loading, respectively (Table II). The PES-CTBN-PES copolymer-toughened epoxy samples exhibited two T_g values instead of three, which was possibly due to the very similar T_g values of PES and the epoxy resin. Therefore, the lower T_g was considered to be from the CTBN domain while the higher one was believed to have resulted from the PES and epoxy resin.

**Figure 3** GPC profile of PES-CTBN-PES copolymer.

The decreased higher T_g with loading could be due to the phase mixing of the epoxy resin with PES and possibly also with CTBN, and the decreased lower T_g could be attributed to increased phase separation of CTBN with higher loading. A similar behavior was observed in the epoxy samples toughened by the CTBN/8K PES blend, PES, and CTBN, as shown in Table II. The 15K PES-CTBN-PES copolymer-toughened epoxy samples exhibited very similar thermal behavior but slightly lower T_g and degradation started at a lower temperature than for the 20K PES-CTBN-PES toughened epoxy samples.

The toughened epoxy samples exhibited slightly lower initial decomposition temperatures than the control samples but had similar degradation behavior (Fig. 5). Among the toughened samples, the PES-toughened samples showed the best thermal stability at 500°C, followed by the copolymer-toughened samples, CTBN/8K PES blend-toughened samples, and CTBN-toughened samples. At 650°C all samples were completely

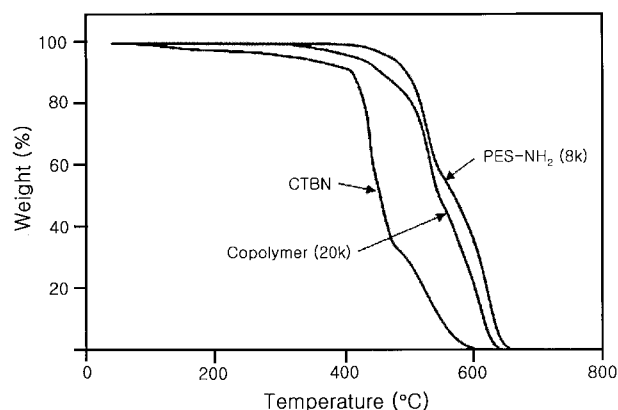
**Figure 4** TGA of PES-CTBN-PES copolymer.

Table II Glass-Transition Temperature (T_g) of Toughened Epoxy Resins

Loading (wt %)	T_g (°C)			
	CTBN	PES-NH ₂ (8K)	Blend (CTBN + 8K PES, 1 : 2)	Copolymer (20K) (PES-CTBN-PES)
0	223	223	223	223
10	-10,213	217	-9,214	-9,218
20	-15,185	215	-13,209	-12,217
30	—	204	-18,197	-15,208

As measured by DMA at 5°C/min.

burned. Therefore, it can be said that the thermal stability of the epoxy resin did not deteriorate from PES-CTBN-PES copolymer toughening, although the initial decomposition temperature was slightly lowered.

Mechanical Properties of Toughened Epoxy Resins

Fracture Toughness

The PES-CTBN-PES copolymers (15K and 20K), CTBN/8K PES blend, and PES-NH₂ (8K) were soluble in epoxy resin up to 40 wt % without a solvent, but the solubility of CTBN in the epoxy was only 20 wt %. The K_{IC} of the epoxy control sample was 0.56 MPa m^{0.5}, but it was remarkably enhanced by 20K PES-CTBN-PES copolymer toughening (2.33 MPa m^{0.5}) at 40 wt % loading (Fig. 6). These values were higher than those reported previously with amine-terminated 20K PES.¹⁶ The epoxy resins toughened with the CTBN/8K PES blend exhibited slightly lower fracture toughness (1.82 MPa m^{0.5} at 40 wt %)

than the copolymer-toughened samples, followed by the 8K PES oligomer (1.54 MPa m^{0.5} at 40 wt %) and CTBN (1.07 MPa m^{0.5} at 20 wt %), demonstrating the excellence of the copolymer toughening.

The 15K PES-CTBN-PES copolymer toughening provided a fracture toughness of 2.21 MPa m^{0.5}, which was slightly lower than that with the 20K PES-CTBN-PES copolymer (2.33 MPa m^{0.5}), demonstrating the effect of the molecular weight. As reported by Kim et al.,²⁴ toughening with the CTBN/PES blend exerted a synergistic affect and provided almost the same fracture toughness as the copolymer toughening at low loadings. However, at 25 wt % or higher loadings, the copolymer toughening exhibited a much higher K_{IC} than CTBN/8K PES blend toughening (Fig. 6), which was possibly attributable to the chemical bonds between the PES-CTBN-PES copolymer and the epoxy resin.

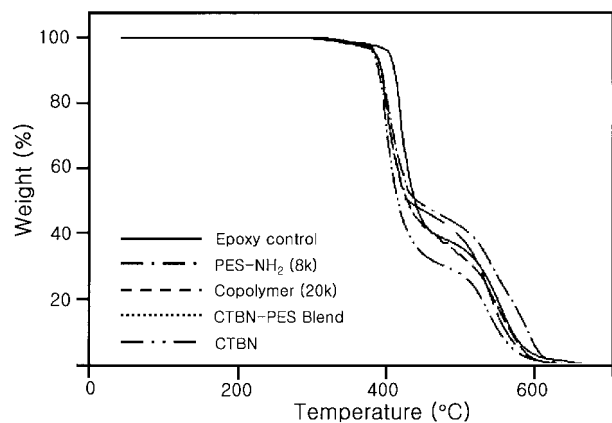


Figure 5 TGA of 20k PES-CTBN-PES toughened epoxy resins.

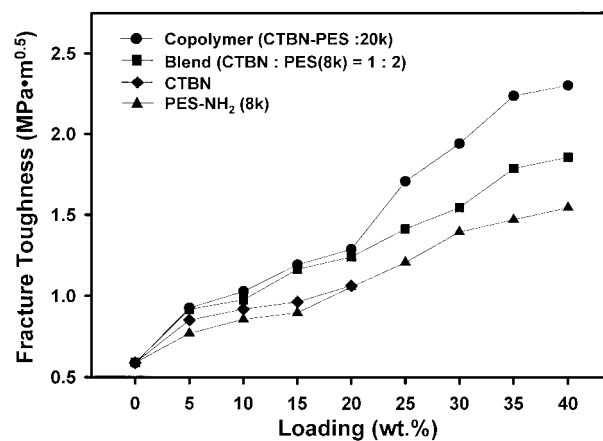


Figure 6 K_{IC} fracture toughness of 20k PES-CTBN-PES toughened epoxy resins.

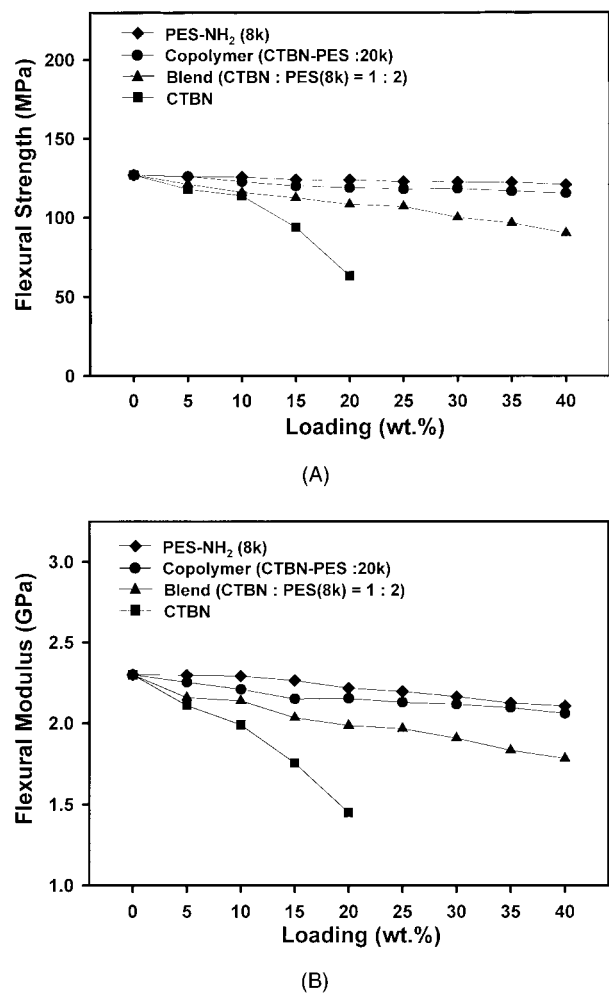


Figure 7 Flexural properties of 20k PES-CTBN-PES toughened epoxy resins A) Flexural strength, B) Flexural modulus.

Flexural Properties

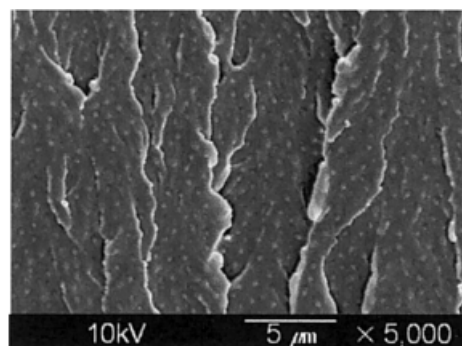
As expected, the PES-toughened epoxy resins resulted in the smallest drop in the flexural strength and flexural modulus, followed by the 20K PES-CTBN-PES and the 15K PES-CTBN-PES copolymers, the CTBN/8K PES blend, and CTBN, as shown in Figure 7. The flexural strength and flexural modulus of the control samples were 127 MPa and 2.3 GPa, respectively, and they decreased with toughener loading. The flexural strength and flexural modulus of the epoxy resin were essentially unaffected by the incorporation of PES-NH₂ (8K) and were 120 MPa and 2.1 GPa at 40 wt %, respectively. However, the 20K PES-CTBN-PES copolymer and the 15K PES-CTBN-PES copolymer-toughened epoxy samples showed flexural strengths of 115 and 111 MPa

and flexural moduli of 2.0 and 2.0 GPa at 40 wt %, respectively, while the CTBN/8K PES blend-toughened epoxy sample showed a flexural strength of 90 MPa and a flexural modulus of 1.8 GPa at 40 wt %. The CTBN-toughened epoxy samples showed a considerable drop in the flexural strength (63 MPa) and flexural modulus (1.4 GPa) even at 20 wt %, which could be attributed to the soft rubber modifier.

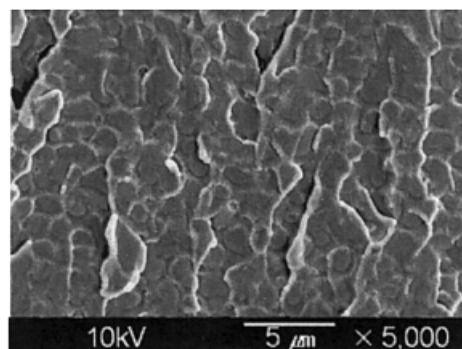
Fracture Surface Analysis by SEM

The 8K PES-toughened epoxy samples showed a second phase on the order of 0.5 μ m, which was possibly PES spheres at low loadings [Fig. 8(A)], but a PES continuous phase at 30 and 40 wt % loadings [Fig. 8(B)]. Therefore, the increased fracture toughness with 8K PES could be attributed to the ductile fracture of PES continuous phases and to the chemical bonds between PES and the epoxy resin as reported previously.^{16,17}

The CTBN-toughened epoxy samples showed a second phase that was 3–5 μ m in size at 5–15 wt

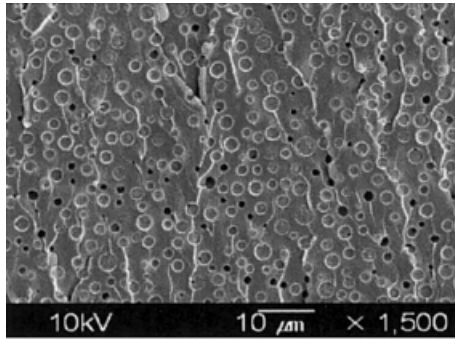


(A)

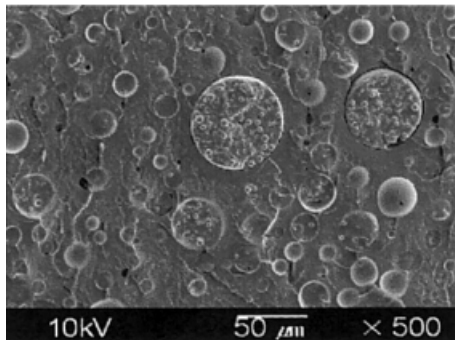


(B)

Figure 8 SEM micrographs of 8k PES toughened epoxy samples, A) 20 wt %, B) 30 wt %.



(A)



(B)

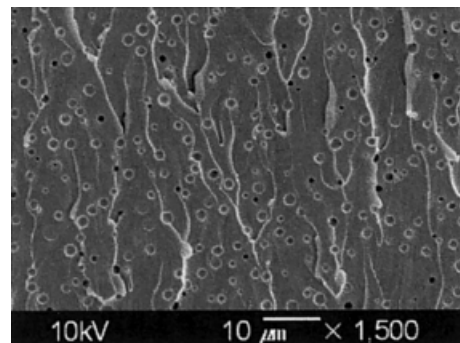
Figure 9 SEM micrographs of CTBN toughened epoxy samples, A) 10 wt %, B) 20 wt %.

% loading [Fig. 9(A)] but exhibited up to 50- μm particles at 20 wt % loading [Fig. 10(B)]. In addition, a third phase was observed from the second phase particles at 20 wt % loading while some large particles could be seen at 5–15 wt % loading. At 10 wt % loading approximately half of the fracture surface was covered by the second phase. Therefore, it can be said that the second phase is a mixture of rubber and epoxy, and some areas contain a much higher rubber content than others. Thus, it is believed that the holes on the fracture surface were formed by the cavitation of the second phase that contained high rubber content. At 20 wt % of CTBN loading the surface of the second phase was clean and there was a gap between the matrix and the second phase particles, indicating poor adhesion between these two phases.

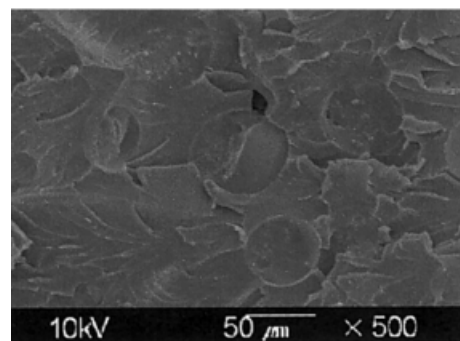
The epoxy samples modified by the CTBN/8K PES blend (1:2) showed small second phase particles that were 2–3 μm in size at 10–20 wt % loading and 30–50 μm particles at 30–40 wt % loading (Fig. 10). At higher loadings the third

phase particles were also observed on the fracture surface of the second phase, as observed from CTBN-modified epoxy samples. On the fracture surface some of the second phase particles showed clean surfaces, indicating poor adhesion between the matrix and second phase particles. This could be explained by the poor phase mixing between CTBN and the epoxy resin at 20–40 wt % loadings. Poor phase mixing, and thus poor adhesion, may be responsible for the lower fracture toughness and flexural properties compared to the 20K PES-CTBN-PES copolymer-toughened samples.

The 20K PES-CTBN-PES copolymer-toughened epoxy samples showed evenly dispersed second phase particles (1–2 μ) at 10 and 20 wt % loading [Fig. 11(A)]. However, a PES continuous morphology (phase inverted morphology) was also observed, similar to the 8K PES-toughened samples [Fig. 8(B)], with the exception of some deep holes. An analysis at high magnification revealed that there seemed to be three phases: a continuous PES-rich phase, a discrete epoxy-rich phase,

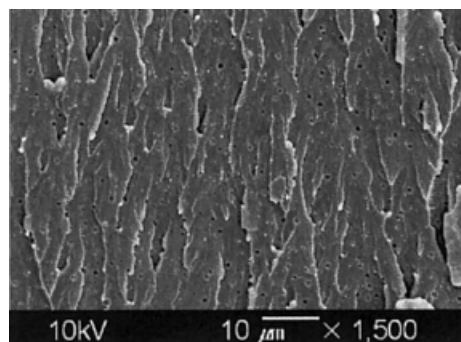


(A)

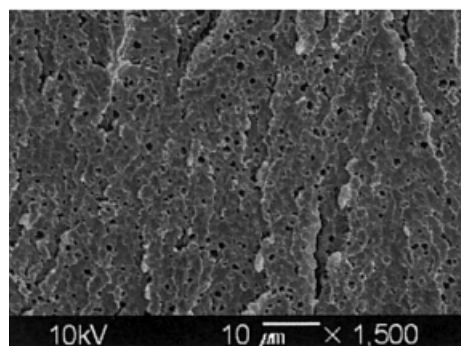


(B)

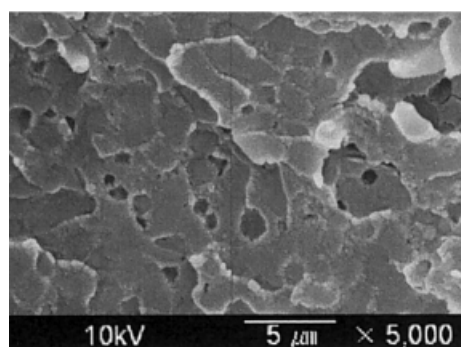
Figure 10 SEM micrographs of CTBN/8kPES blend toughened epoxy samples A) 10 wt % (1500 \times), B) 40 wt % (400 \times).



(A)



(B)



(C)

Figure 11 SEM micrographs of 20k PES-CTBN-PES copolymer toughened epoxy samples A) 10 wt % (1500 \times), B) 40 wt % (1500 \times), C) 40 wt % (5,000 \times).

and a rubber-rich phase [Fig. 11(C)]. In other words, the epoxy-rich phase and the rubber-rich phase are surrounded by the continuous PES-rich phase, and the rubber-rich phase forms deep holes by cavitation upon fracture. Therefore, the main toughening mechanism operating in the PES-CTBN-PES copolymer-toughened epoxy system is believed to be the ductile fracture of the

PES-rich phase and the cavitation of the CTBN-rich phase. The epoxy samples toughened with the 15K copolymer also exhibited phase separation behavior similar to that of the 20K copolymer-toughened epoxy resin, but the lower fracture toughness obtained can be attributed to the lower molecular weight of the 15K copolymer.

Solvent Resistance

The amine-terminated PES or the PES-CTBN-PES copolymer-toughened epoxy resins exhibited excellent solvent resistance in chloroform; no change in color or shape was observed after being immersed in CH_2Cl_2 for 3 days, even at 40 wt % loading (Table III). In the SEM analysis no sign of dissolution was detected from the copolymer-toughened epoxy sample, indicating excellent chemical resistance arising from the chemical bonds between the amine-terminated tougheners (PES-CTBN-PES copolymer) and the epoxy resin. However, CTBN or CTBN/PES blend-toughened epoxy samples exhibited poor chemical resistance in chloroform. The dissolution of the CTBN phase, as well as the disintegration of whole samples at high loadings, occurred because of the absence of chemical bonds between the epoxy resin and CTBN. Therefore, the chemical bonds between the toughener and the epoxy resin could be the key factor in improving the chemical resistance of toughened epoxy resins.

CONCLUSIONS

DGEBA-based epoxy resins were toughened with amine-terminated PES-CTBN-PES triblock copolymers, which were prepared from amine-terminated PES oligomers and a commercial CTBN

Table III Solvent Resistance of Toughened Epoxy Resins

Loading (wt %)	PES-NH ₂ CTBN	PES-NH ₂ (8K)	Blend (CTBN + 8K PES, 1 : 2)	Copolymer (20K) (PES-CTBN-PES)
10	I	I	I	I
20	D	I	I	I
30	—	I	D	I
40	—	I	D	I

As measured in CHCl_3 at 25 $^\circ\text{C}$ after 3 days; I, insoluble; D, disintegration.

rubber. The fracture toughness, thermal and flexural properties, and solvent resistance were evaluated and compared to samples toughened by a CTBN/PES blend, PES, or CTBN. The major findings are summarized below:

1. The amine-terminated PES-CTBN-PES triblock copolymers were successfully synthesized from the amine-terminated PES and a commercial CTBN rubber, which was confirmed by end-group titration, thermal analysis, FTIR, GPC, and viscosity measurements.
2. A K_{IC} value of 2.33 MPa m^{0.5} was obtained with the amine-terminated 20K PES-CTBN-PES copolymer at 40 wt % loading without sacrificing mechanical properties, solvent resistance, and thermal properties. However, toughening with the CTBN/8K PES blend, CTBN, and 8K PES provided lower a K_{IC} and lowered the thermal and flexural properties, as well as the solvent resistance.
3. The significant enhancement of the fracture toughness with the amine-terminated PES-CTBN-PES copolymer toughening could be attributed to the ductile fracture of the PES-rich continuous phase and the cavitation of the rubber-rich phase, as well as the chemical bond formation between the copolymer and the epoxy resin.

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