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Shan-Jun Li^a; Li-Gui Zhou^a; Yong Chen^a

^a Institute of Material Science Fudan University, Shanghai, China

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TOUGHENING STUDY OF EPOXY RESIN BY THE COPOLYMER OF THE α -METHACRYLATE MONOMER OF POLY(ETHER-SULFONE) WITH *n*-BUTYL ACRYLATE†

SHAN-JUN LI,* LI-GUI ZHOU, and YONG CHEN

Institute of Material Science
Fudan University
Shanghai, China 200433

ABSTRACT

A novel copolymer of the α -methacrylate macromonomer of poly(ether-sulfone) with *n*-butyl acrylate (PES-*n*-MA-*co*-BA) was synthesized for evaluation as a toughening agent in epoxy resins, and characterized by IR, HPLC, and UV. The effects of the copolymer (PES-*n*-MA-*co*-BA) and of blends (PES + PBA) upon the toughening of epoxy resins was investigated by tensile tests and scanning electron microscopy. The optimum content of the functional monomer in the copolymer with *n*BA, which has a maximum improvement of fracture toughness without any significant loss of modulus, was obtained. Studies on the morphology of the modified epoxy resin system with SEM showed that phase separation was observed during curing of both DGEBA/PES-MA-*co*-*n*BA and DGEBA/PnBA/PES systems. The mechanical test results showed that the use of a smaller amount of the copolymer of PES-5-MA and *n*BA or of blends of PES and PnBA leads to an effective toughening of the DGEBA resin. The blending of PES and PnBA as a modifier for epoxy resin is found to be especially promising.

†This paper is dedicated to Dr. Otto Vogl on the occasion of his 65th birthday with our warmest wishes.

INTRODUCTION

Epoxy resins are widely employed as the basis for adhesive compositions and as the matrix material for composites. However, in many applications they have one major drawback: They are brittle and therefore have fairly low impact and fracture strengths. Brittle epoxy resins have been modified successfully with rubber to enhance fracture toughness.

To increase fracture toughness, two methods based upon attaining a second phase dispersion of a polymeric modifier in the epoxy resin have been reported. On the other hand, the second phase is rubbery in character; on the other hand, it is thermoplastic.

Various kinds of rubbers have been used to toughen epoxy resins including reactive butadiene-acrylonitrile oligomers having both carboxyl and amine end groups [1-3], acrylate elastomers [4, 5], polysiloxanes [6], and so on.

For the last several years, our group has been using functionally poly-*n*-butyl acrylate (PnBA) with either an epoxy or carboxyl group to modify the epoxy resin [4]. A major disadvantage of this approach is a lowering of the glass transition temperature and a reduction in the modulus of elasticity and tensile strength.

Many studies have been conducted in the last decade on the toughening of epoxy networks by using tough ductile engineering thermoplastics which seem to provide better improvement in the overall properties of the resulting networks without any significant loss in the modulus. Polyethersulfone (PES) and polyetherimide (PEI) have been used to modify trifunctional and tetrafunctional epoxies by Partridge [7, 8]. McGrath [9] reported that hydroxyl- or amino-terminated PES and amino-terminated polyetherketone (PEK) modified DDS cured Epon 828 systems.

It was therefore the objective of this work to evaluate the effects of a combination of rubbery polymer and ductile thermoplastic polymer on the toughening of an epoxy resin. The rubbery polymer used here was a poly (*n*-butyl acrylate) and the thermoplastic was poly(ether-sulfone). To compare the two toughening results, two approaches of the modified system were investigated.

One approach has been taken to modify the epoxy resins with the ternary blends of the epoxy resins PES and PnBA, and the other approach has been to use the copolymer of the α -methacrylate macromonomer of poly(ether-sulfone) with *n*-butylacrylate.

The present paper describes the synthesis of copolymers of the α -methacrylate macromonomer of poly(ether-sulfone) with *n*-butyl acrylate with different compositions and their toughening studies in modifying epoxy resin. They are compared with ternary blends of PES/PnBA/DGEBA, and the relationship between morphology and mechanical properties is investigated.

EXPERIMENTAL

Materials

4,4'-Dihydroxydiphenyl sulfone (DDS) produced by the Suzhou Resin Plant was recrystallized from aqueous alcohol water (1:4) by volume and has a melting point of 247-248°C. 4,4'-Dichlorophenyl sulfone supplied by the Shanghai No. 9 Dye-Chemical Plant was crystallized twice from aqueous alcohol (1:9) and has a melting point of 148-149°C. 4-Hydroxyl diphenyl sulfone was obtained by the

hydrolysis of 4-chlorodiphenyl sulfone in basic solution and recrystallized from aqueous alcohol (1:4) by volume. Its melting point was 136–138°C. 4-Chlorodiphenyl sulfone was prepared by heating a mixture of *p*-chlorobenzenesulfonyl chloride and chlorobenzene. Azobisisobutyronitrile (AIBN) was recrystallized three times from absolute methanol and dried for 1 day at 0.05 mmHg at room temperature. *n*-Butyl acrylate (BA) was distilled under reduced pressure (20 mmHg) before use. Tetramethylammoniumbromide ((CH₃)₄NBr), methacryloyl chloride (from Aldrich Chemical Co.), and 4,4'-diaminodiphenylmethane (DDM) were used without further purification. Solvents such as dimethylsulfoxide (DMSO), 1-butanol, and dichloromethane were used as received. The poly(ether-sulfone) (PES) was supplied by the Shanghai Suguan Chemical Work. The epoxy resin employed was the diglycidyl ether of Bisphenol A obtained from the Shanghai Resin Plant. The titrated equivalent weight of the resin was 190 g/equiv.

Measurements

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer on solid samples as potassium bromide pellets. ¹³C-NMR spectra were recorded on a Bruker spectrometer with complete proton decoupling; TMS was used as the internal standard. Ultraviolet absorptions were measured on a DU-7 spectrophotometer (Beckman Co.) in chloroform solution. Microanalyses were carried out in the Microanalytical Laboratory, Department of Chemistry, Fudan University. The relative molecular weights of the poly(ether-sulfone) oligomers and its copolymers with BA were measured by GPC in tetrahydrofuran at 25°C, with polystyrene as the calibration standard. The viscosity-average molecular weights were determined by using an Ubbelohde viscometer in acetone at 25°C. The tensile toughness test was carried out on an Instron 1121 instrument loaded 1000 N at a crosshead speed of 50 mm/min. Tensile strength and Young's modulus were obtained simultaneously by this test. The tensile impact energy was calculated from the area under the stress-strain curve [4]. The morphologies of the impact fracture surfaces of the samples were observed by using a scanning electron microscopy (SEM) after they were coated with a layer of gold about 200 Å thick.

Synthesis

1. *Potassium Salt Formation.* The phenols used in these experiments were in the form of potassium salts. They were made by dissolving the corresponding phenols in methanol and titrating potentiometrically with 4 N potassium hydroxide. The salts obtained after evaporation of the solvent were dried under vacuum.

2. *The Synthesis and Characterization of α -Hydroxyl-terminated Poly-(Ether-sulfone) Oligomers* [10]. The hydroxyl-terminated poly(ether-sulfone) oligomers in Table 1 were prepared as follows. A 250-mL three-necked flask was fitted with a mechanical stirrer, a condenser, a thermometer, and a nitrogen inlet tube. Fifty milliliters of dimethyl sulfoxide, 4,4'-dichlorodiphenyl sulfone (10.34 g, 0.036 mol), and 4-hydroxyl diphenyl sulfone K-salt (2.8 g, 0.008 mol) were added to the flask. The flask was quickly heated in an oil bath to 145 ± 1°C. Then 4,4'-dihydroxyl diphenyl sulfone K-salt (11.12 g, 0.036 mol) was divided into four parts. The parts were added individually about every 15 min, and the temperature

TABLE 1. Preparation of Hydroxyl-Terminated Poly(Ether-sulfone) Oligomers^a

No.	N_s/N_0	Calculated $M_w \times 10^{-3}$	GPC peak RT (min)	$M_\eta \times 10^{-3}$ g/mol
PES-1	0	$1 \times M_0$	61	
PES-5	1/2	$5 \times M_0$	56	1.16
PES-10	2/9	$10 \times M_0$	49	2.45

^a M_η = viscosity-average molecular weight.

RT = retention time.

M_0 = molecular weight of monomer.

was maintained at 145°C for 3 h. It was then raised to 155°C and held there for 1 h. After cooling to room temperature, the product was slowly poured with stirring into 250 mL water which contained 5 g oxalic acid. The oligomer was kept in this acid solution overnight. The filtered product was washed with distilled water and dried.

The average degree of polymerization of the oligomers \bar{X}_n can be defined by the simple equation

$$\bar{X}_n = (2N_0 + N_s)/N_s$$

where N_0 is the number of moles of the potassium salt of 4,4'-dihydroxydiphenyl sulfone and N_s is the number of moles of the potassium salt of 4-hydroxydiphenyl sulfone.

PES-10 was prepared essentially by the same way as PES-5. The preparation and characterization of some α -hydroxyl-terminated poly(ether-sulfone) oligomers are shown in Table 1.

3. *α -Methacrylate Macromonomer of Poly(Ether-sulfone)* [11, 12]. 4-Hydroxydiphenyl sulfone methacrylate (HDSMA) was prepared as follows: A 250-mL three-necked flask equipped with a mechanical stirrer and an addition funnel, into which was placed pure 4-hydroxydiphenyl sulfone (0.005 mol) and sodium hydroxide (4.5 g) in water (30 mL). The mixture was stirred at room temperature until all the 4-hydroxyl diphenyl sulfone was in solution. Tetramethyl ammonium-bromide was slowly added with stirring. Methacryloyl chloride (1.5 mL) in dichloromethane (20 mL) was placed in the dropping funnel and then added dropwise with vigorous stirring over a period of 30 min at room temperature into the above solution. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h, dried with anhydrous $MgSO_4$, and the dichloromethane was removed on a rotary evaporator. Crude HDSMA was recrystallized from absolute ethanol as white crystals with a melting point of 116.5–117.5°C (determined on an optical melting apparatus at a heating rate of 2°C/min; uncorrected). It was recovered in 84% yield.

Analysis: Calculated for $C_{16}H_{14}O_4$: C, 63.56; H, 4.67. Found: C, 63.32; H, 4.68. The IR spectra of HDSMA showed a carbonyl absorption at 1742 cm^{-1} and no absorption in the region of the hydroxy group (Fig. 1).

The ^{13}C -NMR chemical shift data are presented in Table 2 and the spectrum in Fig. 2. The esterifications of PES-5 and PES-10 with methacryloyl chloride followed the same procedure as mentioned above for HDSMA. Figure 3 is the IR spectrum of PES-5 oligomer; it reveals aromatic hydroxyl absorption at 3372 cm^{-1} . Figure 4 is the spectrum of PES-5-MA; it shows carbonyl absorption at 1755 cm^{-1} and no absorption in the region of the hydroxyl group.

4. *Polymerization of n-Butyl Acrylate* [13]. In a 500-mL three-neck flask with stirrer, condenser, thermometer, and nitrogen inlet tube were placed 200 mL *n*-butanol, 15 mL *n*-butyl acrylate, and 0.4 g AIBN under nitrogen atmosphere. The temperature was rapidly raised to 80°C ($\pm 0.5^\circ\text{C}$) and maintained at this level for 4 h. The reactant was distilled under reduced pressure below 60°C to remove *n*-butanol. The polymer was precipitated by pouring the solution into an appropriate volume of methanol-water solution (volume ratio 2:1). The precipitate was acetone-washed four times. After drying overnight in vacuum at 60°C , the product was a viscous material.

5. *Copolymerization of α -Methacrylate Macromonomer of Poly(Ether-sulfone) with n-Butyl Acrylate*. All the copolymers presented in this work were prepared by essentially the same procedure as was used for the polymerization of nBA. Characterizations of HDSMA-co-nBA and PES-5-MA-co-nBA are given in Table 2. The compositions of all copolymers were established by measurements of the ultraviolet spectra of the polymers. The molecular weights and distributions were characterized with GPC.

Preparation of Fracture Toughness Specimens

All the blends were prepared by a hot melt. Sheets of the blends were prepared by first adding the toughening agent (PnBa, copolymer, or PES) to the DGEBA resin. This mixture was then heated to $130\text{--}140^\circ\text{C}$ in an oil bath and stirred for 5 min. When the mixture had cooled to below 130°C , the DDM curing agent was mixed and stirred by hand for 5 min. Then the resin mixture was degassed in a vacuum at $70\text{--}80^\circ\text{C}$ until most of the entrapped air had been removed. After that, the mixture was poured into a polytetrafluoroethylene mold and cured at 90°C for 3 h. The blend was polished by grinder and post-cured at 160°C for 2 h.

RESULTS AND DISCUSSION

Preparation of Copolymer of PES-MA with BA

The monomer HDSMA and macromer α -methacrylate poly(ether-sulfone) (PES-5-MA and PES-10-MA) were copolymerized with BA (initiator: AIBN). The copolymer were obtained in good yields with molecular weights of about 2×10^4 , except for PES-10-MA(10%)-co-BA which had a molecular weight up to 3.35×10^4 .

The copolymerizations of HDSMA were carried out with feed ratios of 5, 10, 15, and 20 phw of HDSMA in the mixtures. The functional comonomer HDSMA was incorporated in 3.13, 6.54, 16.8, and 18.89 mol%, respectively. The copolymerization of 5 and 10 phw of PES-5-MA with BA gave polymers with the incorpora-

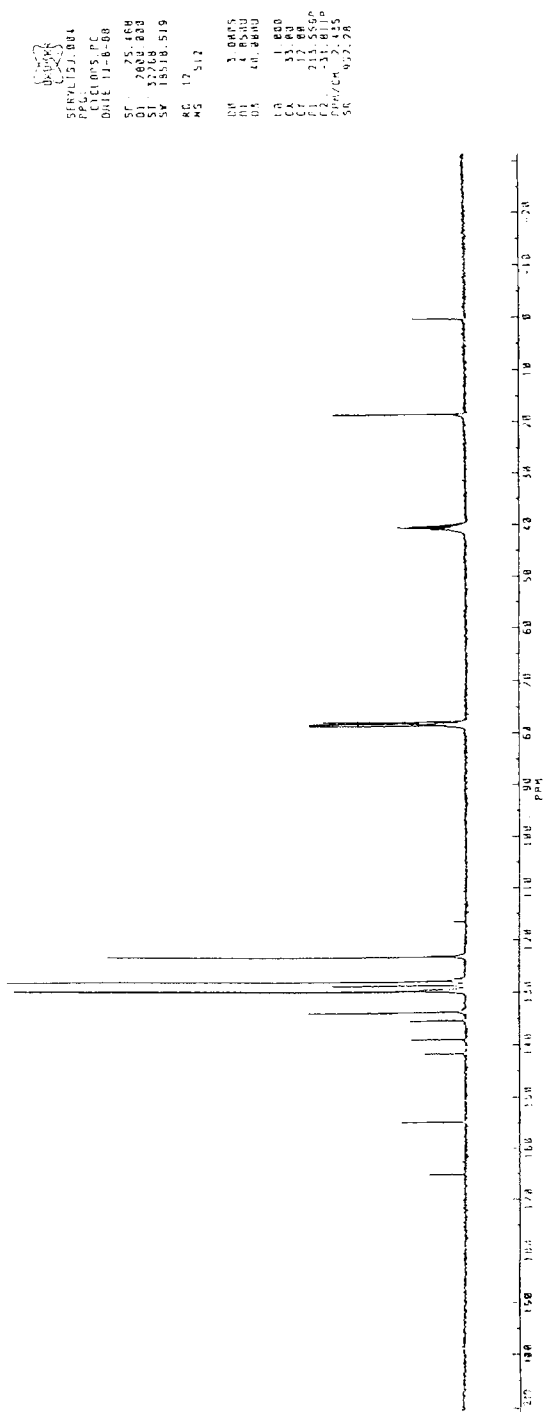


FIG. 1. ^{13}C NMR of 4-hydroxydiphenyl sulfone methacrylate (HDSMA).

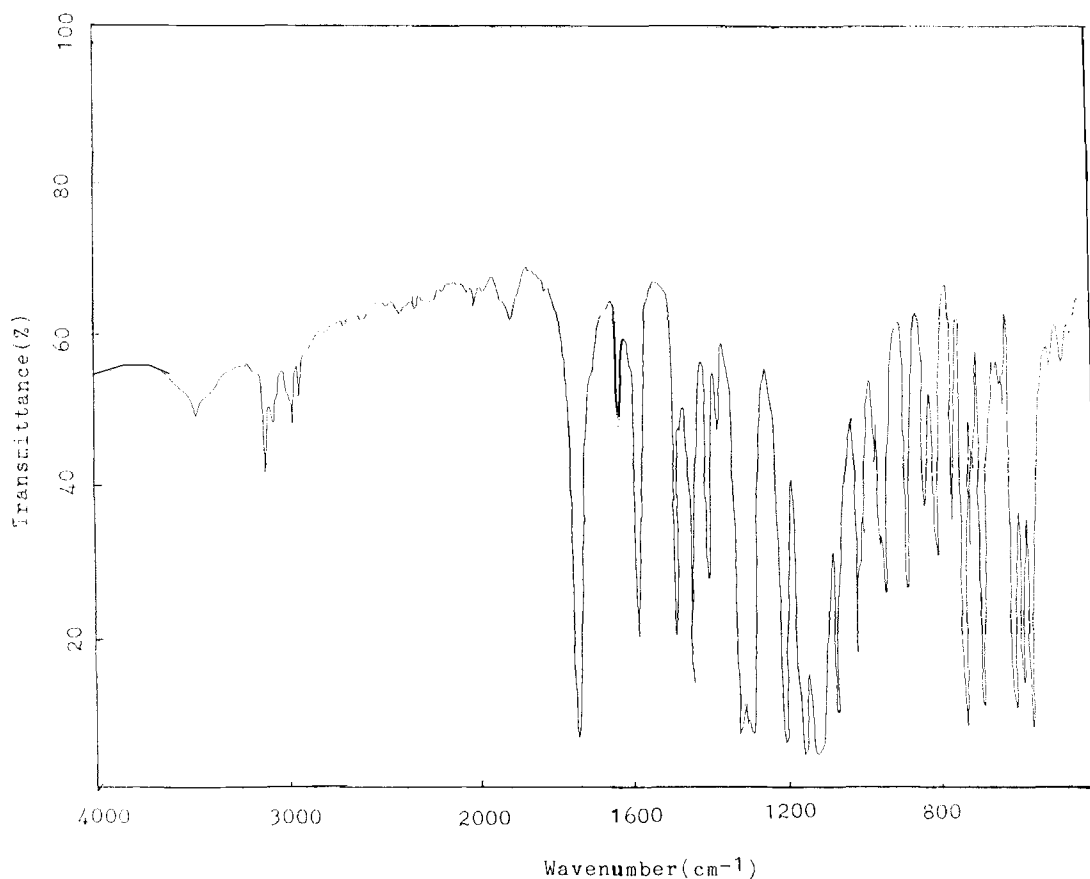


FIG. 2. IR of 4-hydroxydiphenyl sulfone methacrylate (HDSMA).

tion of 6.36 and 9.47 phw of PES-5-MA. The copolymerization of 10 phw PES-10-MA with BA had 12.71 mol% of PES-10-MA comonomer unit in the polymer. All results of copolymerizations of HDSMA, PES-5-MA, and PES-10-MA showed that α -methacrylate poly(ether-sulfone) macromer has high reactivity.

Mechanical Properties of DGEBA/HDSMA-co-BA Blends

The mechanical properties of modified DGEBA with HDSMA-co-BA copolymers are shown in Table 3. There is an initial increase in tensile fracture energy, tensile strength, and elongation with increasing mol fraction of HDSMA, and the maximum value at 5 mol% HDSMA is a 2.7-fold increase in tensile fracture energy than that of the control. The tensile modulus of the blends exhibits a linear increase with HDSMA. An advantage of this modified system is that it apparently improved fracture toughness without significantly decreasing the tensile modulus.

Examination of the fractures surface in the SEM showed the presence of HDSMA in poly(HDSMA-co-BA) modified DGEBA, as illustrated in Fig. 6. All these samples reveal the formation of a spherical domain dispersed in the cross-linked matrix. The increase of HDSMA concentration in poly(HDSMA-co-BA)

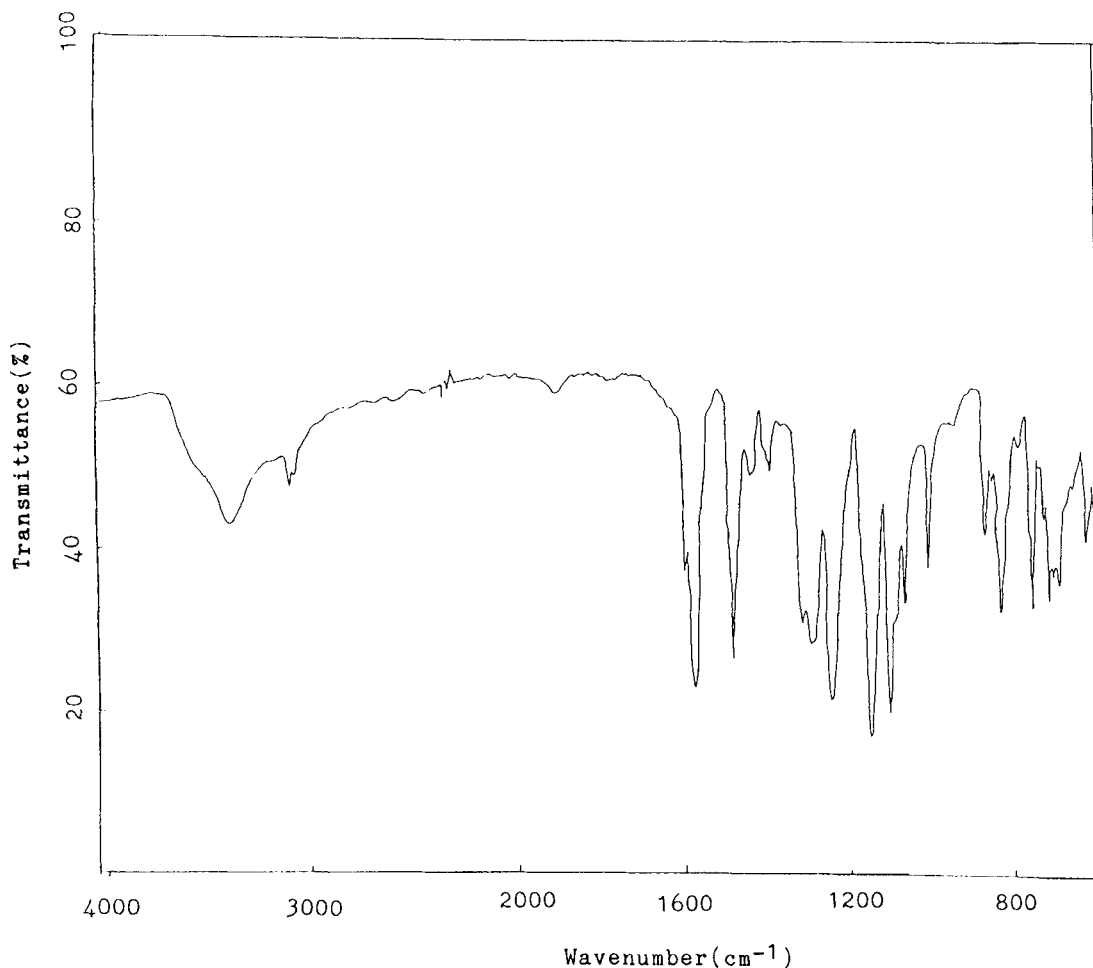


FIG. 3. IR of PES-5 oligomer.

elastomers gave rise to an increase in the number of particles and a decrease in the diameter of the particles. We consider this to be due to the improvement of compatibility between DGEBA and poly(HDSMA-*co*-nBA) with increasing HD-SMA concentration.

In studies on the effect of rubber content on modified epoxy systems with *n*-butyl acrylate it was found that HDSMA(5%)-*co*-BA were utilized as modifiers at levels of 5, 10, and 15% by weight. Table 4 summarizes data on the mechanical properties of modified DGEBA blends. The results of DGEBA/PnBA blends are also listed.

Table 4 shows the improvement of fracture toughness and the existence of an optimum content for all these blends. With the addition of phw content of HDSMA(5%)-*co*-BA and PES-5-MA(5%)-*co*-BA into DGEBA, the fracture toughness increased by 1.7 and 2.4 times that of the control respectively. However, for the DGEBA/PnBA blends, an optimum content of 8 phw shows a 1.5-fold increase. This result is essentially consistent with that of DGEBA modified by PnBA containing a polyfunctional epoxy group, as reported in our previously work [4].

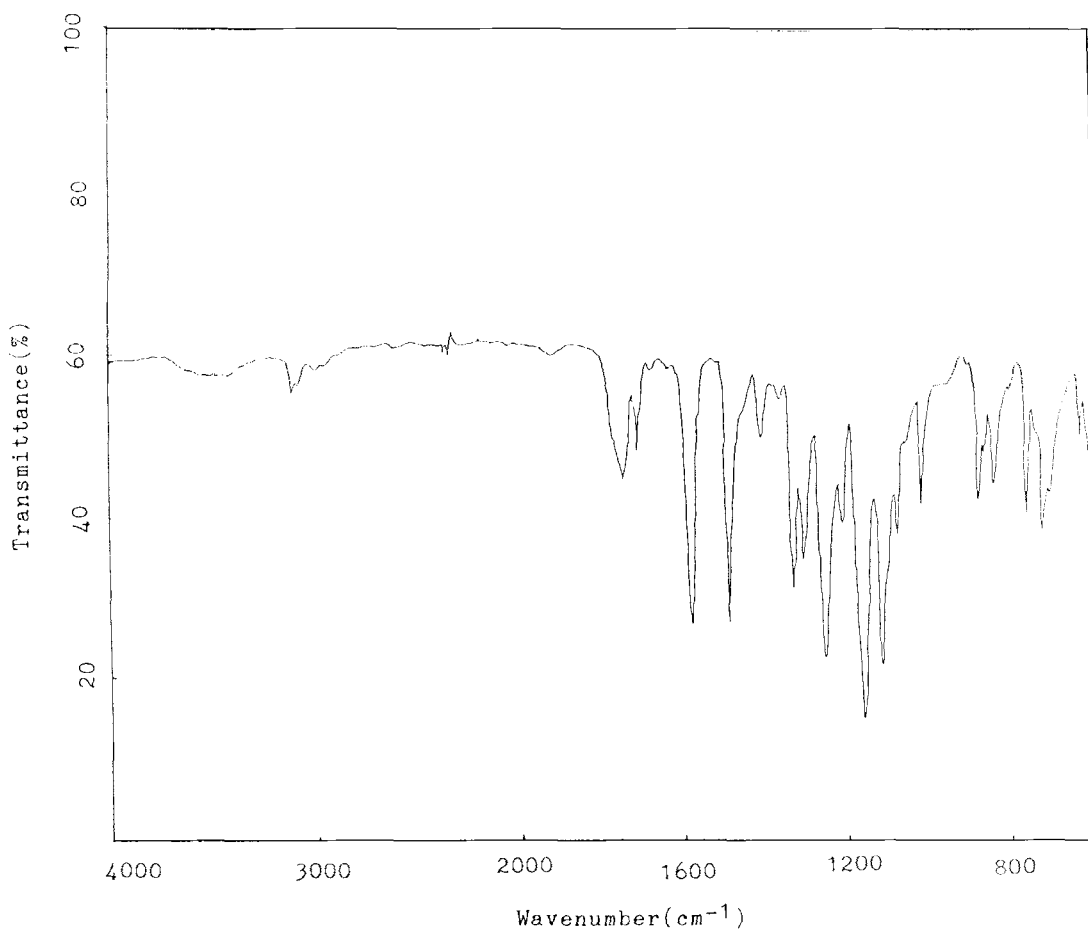


FIG. 4. IR of PES-5-MA macromer.

TABLE 2. Characterization of Copolymers of α -Methacrylate Poly(Ether-sulfone) Macromer-*n*-Butyl Acrylate

Sample	Maximum (nm)	PES % found	$M_n \times 10^{-4}$ (GPC)	d (μm) ^a
HDSMA(5%)- <i>co</i> -BA	250.0	3.13	2.10	2.5
HDSMA(10%)- <i>co</i> -BA	250.0	6.54	1.91	2.7
HDSMA(15%)- <i>co</i> -BA	250.5	16.80	2.42	1.7
HDSMA(20%)- <i>co</i> -BA	250.5	18.69	2.39	1.9
PES-5-MA(5%)- <i>co</i> -BA	264.5	6.36	2.19	1.9
PES-5-MA(10%)- <i>co</i> -BA	262.0	9.47	2.25	2.0
PES-10-MA(10%)- <i>co</i> -BA	265.5	12.71	3.35	2.0

^a d = diameter of particle.

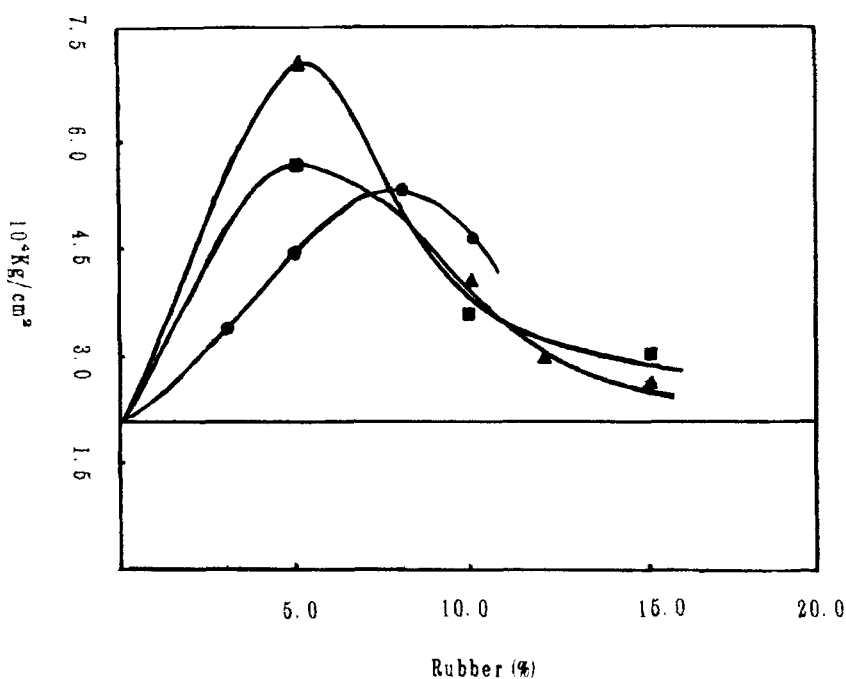


FIG. 5. Fracture toughness as a function of weight fraction of elastomers. (●) PnBA, (■) HDSMA-co-BA, (▲) PES-5-MA-co-BA.

TABLE 3. The Mechanical Properties of the Copolymer HDSMA-nBA as a Function of HDSMA Content^a

Rubber	Eu (%)	$\sigma \times 10^{-2}$ kg/cm ²	$FT \times 10^4$ J/m ²	$E \times 10^{-4}$ kg/cm ²	d (μ m)
HDSMA(5%)-co-BA	5.33	6.73	5.57	1.26	2.5
HDSMA(10%)-co-BA	4.17	5.66	3.83	1.36	2.5
HDSMA(15%)-co-BA	3.83	5.40	3.79	1.41	2.3
HDSMA(20%)-co-BA	2.33	3.84	2.31	1.65	2.5
PES-5-MA(5%)-co-BA	5.27	6.79	7.04	1.31	3.8
PES-5-MA(10%)-co-BA	3.67	5.21	3.39	1.42	2.8
PBA	5.00	5.50	4.41	1.10	2.5

^a Eu = ultimate elongation.

σ = tensile strength.

FT = fracture toughness.

E = Young's modulus.

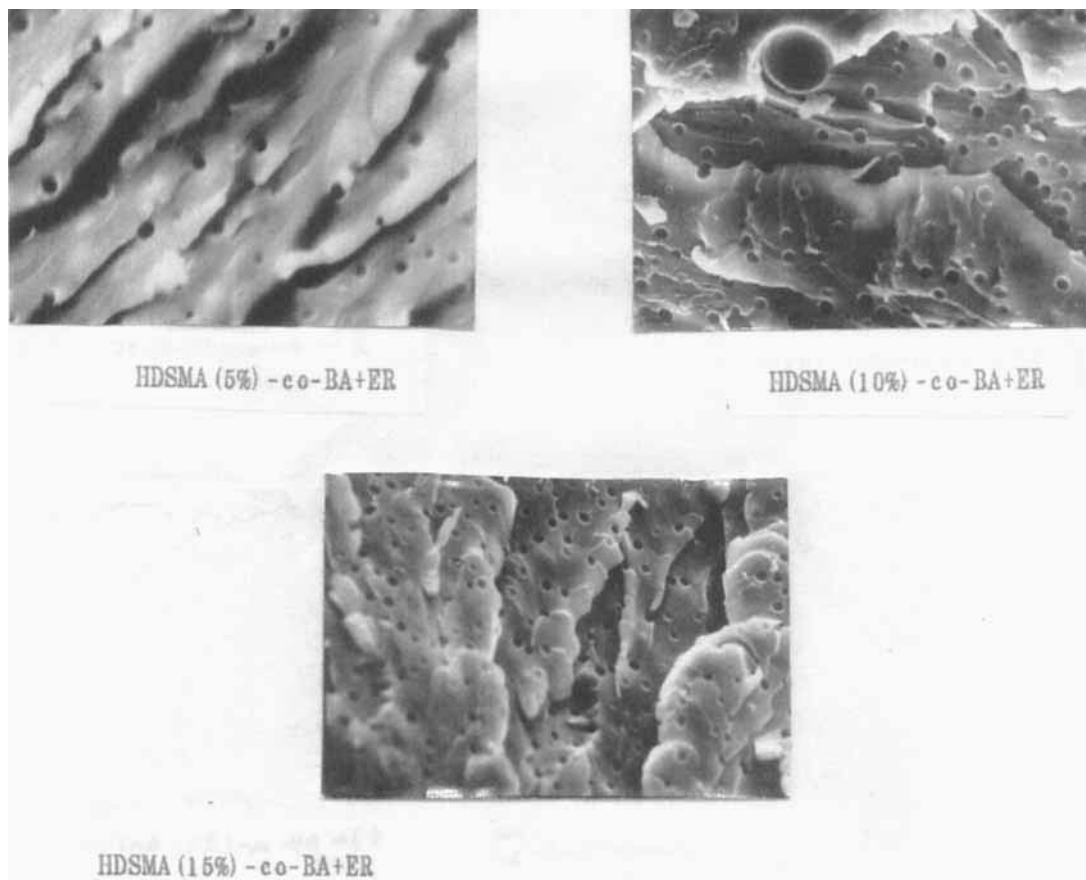


FIG. 6. Fracture surface of modified epoxy resin with HDSMA-co-BA.

In addition, the tensile modulus increases sharply with increasing content of HDSMA(5%)-co-BA and PES-5-MA(5%)-co-BA. A SEM micrograph of PES-5-MA(5%)-co-BA, shown in Fig. 7, exhibits a phase separation structure.

This study suggests that the amount of rubbers used in this system was much less than that of low molecular weight RLP (reactive liquid polymer), which is generally in the range of 10–20 phw, as reported previously [14, 15]. This means that the addition of a smaller amount of copolymer of α -methacrylate poly(ether-sulfone) macromer and *n*-butyl acrylate of medium molecular weight results in a significant improvement in the overall mechanical properties of the resulting networks systems without any significant loss in modulus.

Toughening of Epoxy Resin with PnBA and α -Hydroxyl-terminated Poly(Ether-sulfone) Oligomers (PES)

The effect of α -hydroxyl-terminated poly(ether-sulfone) oligomers on the epoxy resin system modified with PnBA has been investigated. The results of the fracture energy of ternary blends with various molecular weights of PES are listed in Table 5. The proportion of PnBA and PES was held constant at 95 to 5 by

TABLE 4. The Mechanical Properties of Various Elastomers as a Function of Weight Fraction of Elastomers

Rubber	Pbw	<i>Eu</i> (%)	$\sigma \times 10^{-2}$ kg/cm ²	$FT \times 10^{-4}$ J/m ²	$E \times 10^{-4}$ kg/cm ²
PnBA	0	3.17	5.29	2.07	1.67
	3	4.67	5.40	4.35	1.16
	5	5.00	5.50	4.41	1.10
	8	5.50	5.58	5.26	1.01
	10	5.00	5.44	4.51	1.00
HDSMA- <i>co</i> -BA	5	5.33	6.73	5.57	1.26
	10	3.33	5.46	3.96	1.64
	12	2.88	5.07	2.86	1.76
	15	2.44	3.92	2.63	1.61
PES-5-MA- <i>co</i> -BA	3	5.23	6.70	5.35	1.46
	5	5.27	6.79	7.04	1.31
	10	3.33	5.14	3.54	1.54
	15	2.43	3.19	3.03	1.64

weight in each case. The fracture toughness appears to be sensitive to the molecular weight. In addition, only a small sacrifice in modulus was observed for each modified system. Ternary blends of PnBA, DGEBA, and PES had a 2.2-fold increase of fracture toughness. On the other hand, it was 0.8-fold for the blend of PES-1 and DGEBA and 1.1-fold for the blend of PnBA and DGEBA.

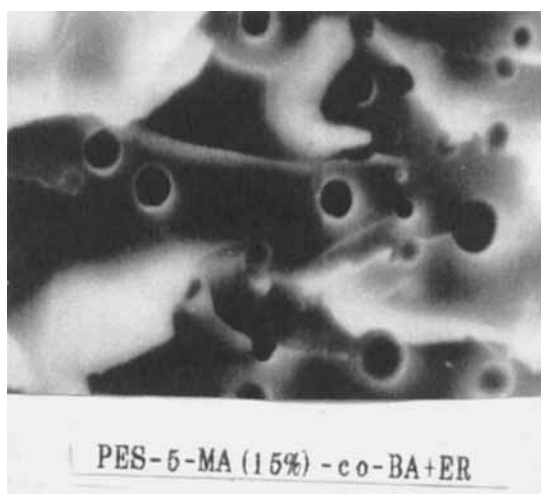


FIG. 7. Fracture surface of modified epoxy resin with PES-5-MA(5%)-*co*-BA.

TABLE 5. Effect of PES with Various Molecular Weights on the Mechanical Properties in Ternary Blends of ER, PES, and PnBA

Sample ^a	<i>Eu</i> (%)	$\sigma \times 10^{-2}$ kg/cm ²	$FT \times 10^{-4}$ J/m ²	$E \times 10^{-4}$ kg/ cm ²	<i>d</i> (μ m)
PES-5 + PBA	5.34	6.87	6.56	1.29	8
PES-10 + PBA	5.00	6.07	4.43	1.22	9
PES-n + PBA	4.00	4.88	3.41	1.22	11
PES-m + PBA	3.83	5.64	3.22	1.47	25
PBA	5.00	5.50	4.41	1.10	2.5
ER	3.17	5.29	2.07	1.67	

^aPES-n = molecular weight of 4,600.

PES-m = molecular weight of 14,400.

DGEBA modified with PES is a homogeneous system (Fig. 8); the system remained essentially transparent. DGEBA modified with PES oligomers and PnBA is heterogeneous. Figure 9 shows SEM micrographs of the fracture surfaces for these ternary blends. The well-defined two-phase morphology can clearly be seen; the size of the rubbery particles increases as the molecular weight of the PES oligomers increase. It might be assumed that the reaction of the hydroxyl groups of PES oligomers with the epoxy ring of DGEBA would take place in the curing process. The lower the molecular weight of PES oligomers and the higher the concentration of the hydroxyl group in the system, the more heat is released. This means that the curing reaction could be accelerated because of the presence of the hydroxyl-terminated group in the PES oligomer; thus, in the reaction of ternary



FIG. 8. Fracture surface of modified epoxy resin with PES.

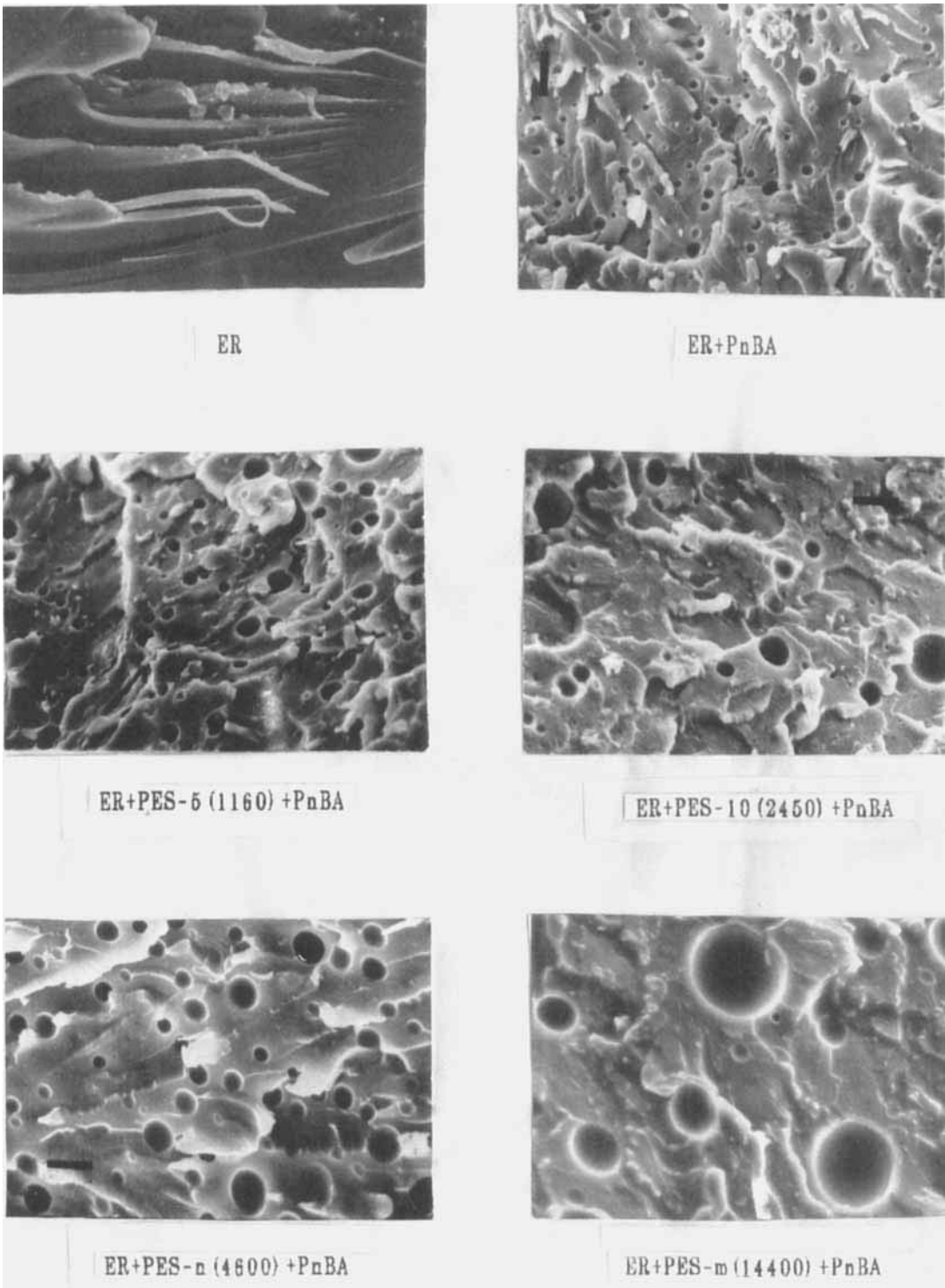


FIG. 9. Fracture surface of modified epoxy resin with PES and PnBA.

TABLE 6. Comparison of Different Toughening Systems

Sample	$\sigma \times 10^{-2}$ kg/cm ²	$E \times 10^{-4}$ kg/cm ²
ER	2.07	1.67
ER + PBA	4.41	1.10
ER + PES-5	3.71	1.42
ER + PES-5 + PBA	6.56	1.29
ER + PES-5-MA(5%)-co-BA	7.04	1.31

blends the addition of PES should facilitate the phase-separate process of PnBA in the epoxy matrix and result in smaller size rubbery particles.

As a consequence, the energy required to break the epoxy resin modified with PnBA is greatly increased by the addition of PES. It is suggested that the effect of PES is similar to that of Bisphenol-A on the toughening of epoxy resin. It was expected that chain extension and perhaps subsequently developed chain entanglements in the modifier might play an important role in the toughening of the networks. Therefore, the effective improvement of fracture toughness for ternary blends of PnBA, PES, and DGEBA presumably arises from the synergistic effect of increasing broken elongation by PES and of yielding stress by PnBA rubber.

Moreover, for modified systems with only poly(ether-sulfone), it has been reported that the addition of poly(ether-sulfone) has little effect upon fracture toughness of the resin mixture, and the fracture toughness of these blends increases with increasing PES molecular weight. In this case, the PES used had a higher molecular weight than the modifiers at the level of 15% by weight. The improvement to toughness in this modified system was explained by the ductile yield of PES [9]. Thus, we believe that PES in DGEBA/PES blends exhibits a different toughening mechanism than PES in DGEBA/PnBA/PES ternary blends because of the presence of PnBA in the system. Additional work on this question using dynamic mechanical analysis is being continued.

Table 6 summarizes the mechanical properties of epoxy resin modified with either copolymers or blends of PnBA and PES. The total content of modifiers was held at the 5% by weight level. It is clear that both the copolymer of PES-5-MA and nBA and the blends of PES and PnBA show effective toughening for the DGEBA resin compared with PES and PnBA, respectively, and the blending of PES and PnBA as a modifier for epoxy resin is more promising.

CONCLUSIONS

1. A series of copolymers of HDSMA, PES-5-MA, and PES-10-MA with nBA was obtained as modifiers for epoxy resin toughening. The results of copolymerization demonstrated that α -methacrylate poly(ether-sulfone) macromer exhibits high reactivity with nBA.

2. It was found that the optimum content of the functional monomer in the copolymer with nBA should be around 5 mol% for DGEBA modified with HDSMA-co-BA and PES-5-MA-co-BA. The addition of 5 phw of these elastomeric copolymers in these blends gives maximum improvement of fracture toughness.
3. The curing systems of both DGEBA/copolymer of α -hydroxyl-terminated poly(ether-sulfone) macromer with nBA and DGEBA/PnBA/PES with DDM show a phase separated structural morphology in SEM results.
4. Use of a smaller amount of the copolymer of PES-5-MA and nBA or blends of PES and PnBA show effective toughening for the DGEBA resin. Blending of PES and PnBA as a modifier for epoxy resin was found to be most promising.
5. Effective improvement of fracture toughness for the ternary blend PnBA/PES/DGEBA presumably arises from the synergistic effect of increasing the breaking elongation by PES and of yielding stress by PnBA rubber.

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