

Toughening of Epoxy Resins with Aromatic Polyesters

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ABSTRACT: Polyesters, prepared by direct polycondensation from bisphenol A and aliphatic dicarboxylic acids [adipic acid (AD), suberic acid, sebacic acid (SE), and dodecanedioic acid], were used to improve the toughness of the diglycidyl ether of the bisphenol A/diaminodiphenyl methane epoxy system. Polyesters had the number average molecular weight (M_n) ranging from 4300 to 19,200 g/mole. The epoxy systems modified with the AD system ($M_n = 6400$ g/mole) and the SE system ($M_n = 10,200$ g/mole) showed phase separated structures with discrete domains of $0.2 \mu\text{m}$, but other systems showed smooth fracture surfaces when observed by scanning electron microscopy. The modified epoxy systems except for the AD system and SE system showed two $\tan \delta$ peaks corresponding to the α and β transitions of the epoxy resin. The modified epoxy systems showed maximum values of K_{1c} at around 10 wt % of polyester and maximum flexural properties at 5 wt % of polyester. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2464–2473, 2000

Key words: epoxy resin; epoxy modifier; epoxy toughening; aromatic polyester; direct polycondensation

INTRODUCTION

Since the first epoxy resin patent was granted in the 1940s, epoxy resins have been used extensively as adhesives and as the matrix resins for fiber reinforced composite materials.^{1–6} Current demands for high performance materials have increased the usefulness of epoxy resins as structural adhesives and as the matrix resins for advanced composites. Both of these applications demand high strength, high modulus, and good adhesion characteristics in the epoxy resins. However, such uses also require good fracture resistance and impact strength, which epoxy resins do not generally exhibit. Therefore, epoxy

resin should be modified by rubber or thermoplastic resin modifier.^{7–14} The principal objective of the rubber modification is the improvement of fracture properties with the smallest possible decrease in modulus and strength. In this study, aromatic polyesters are used as modifiers their effect on the toughness of epoxy resin systems was investigated.

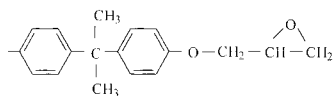
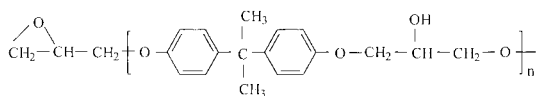
EXPERIMENTAL

Materials

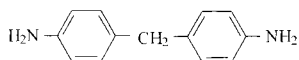
Diglycidyl ether of bisphenol A (DEGBA) type epoxy resin, EPON-828 (Kumho Shell Chemical Co.), and aromatic amine curing agent, 4,4'-diaminodiphenylmethane (DDM, Tokyo Kasei Organic Chemicals), which have chemical structures shown in Figure 1, were used in this study. The

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Diglycidyl ether of bisphenol A (DGEBA)



4,4'-diaminodiphenyl methane (DDM)

Figure 1 Chemical structures of DGEBA and DDM.

epoxy modifiers were prepared by direct polycondensation from bisphenol A and aliphatic dicarboxylic acids [adipic acid (AD), suberic acid (SU), sebacic acid (SE), dodecanedioic acid (DO)]. Triphenylphosphine and hexachloroethane were used as condensing agents. In chlorobenzene, the polyesters were obtained by using acid acceptors such as triethylamine and pyridine. The details of the synthetic procedures followed the Kitayama experimental method.¹⁵ The synthetic route of the polyesters was presented in Figure 2. The synthetic results and physical properties of the polyesters are summarized in Table I.

Preparation of Resin Mixtures

The stoichiometric ratio of DGEBA/DDM (1 : 1) was used as the basis for all resin systems employed in this work. The calculated amount of the aromatic polyester was dissolved in epoxy resin without solvent by heating at 160°C. Then the curing agent, DDM, was added to the mixture, which was kept at 120°C. The resulting clean mixture was cast in an aluminum mold preheated at 120°C. The mixtures cast in different molds were cured in an air-convection oven according to a predetermined schedule described in Table II.

Characterization of Cured Resins

The glass transition temperature (T_g) of the cured epoxy resin was measured by a DSC (Thermal Analyzer Instrument 2910) at a heating rate

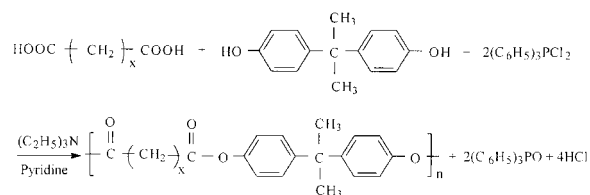
of 10°C/min under N₂ gas. All rheological measurements were carried out using a rheometrics dynamic spectrometer (RDS II, Rheometric Co.) between -150 and 200°C at a heating rate of 5°C/min at frequency of 1 Hz and strain rate of 0.1%. Fracture surfaces were examined on a scanning electron microscope (SEM) (JSM-840A, Jeol Co.). All mechanical tests were carried out on a universal testing machine (Instron 1125, Instron Corp.) at room temperature.

Tensile properties were determined from the dumbbell-shaped specimens according to ASTM D638-86 at a cross-head speed of 5 mm/min. The flexural modulus and strength were measured from three point bending mode according to ASTM D790M-86 at a cross-head speed of 2.0 mm/min. The fracture tests (K_{1c} , G_{1c}) were carried out with small compact tension specimens according to ASTM E399-81. Prior to the testing, the exact dimensions of compact tension specimens were measured and the specimens were precracked by inserting a thin razor length of approximately 3 mm long. In order to prevent crack blunting, a fresh razor blade was used for each specimen: this is one of the standard technique to produce sharp cracks. The specimens were then put into the jig and tested at a cross-head speed of 1.0 mm/min.¹⁶⁻¹⁸

The fracture toughness at crack initiation, in terms of the critical stress intensity factor K_{1c} and the critical strain energy release rate G_{1c} were calculated according to the following equations^{3,17}:

$$K_{1c} = \frac{PY}{BW^{1/2}} \quad (1)$$

and



where $x = 4$: adipic acid (poly-bisphenol A-adipic acid: PBAD)

$x = 6$: suberic acid (poly-bisphenol A-suberic acid: PBSU)

$x = 8$: sebacic acid (poly-bisphenol A-sebacic acid: PBSE)

$x = 10$: dodecanedioic acid (poly-bisphenol A-dodecanedioic acid: PBDO)

Figure 2 Synthetic route to aromatic polyesters.

Table I Properties of Aromatic Polyesters

Code	Polyester	RPM	Yield (%)	$[\eta]^a$ (dL/g)	M_n^b (g/mole)	M_w^b (g/mole)	MWD ^b	T_g^c (°C)
AD-43	PBAD	300	56	0.157	4,300	7,600	1.78	48
AD-64		500	62	0.264	6,400	12,800	1.98	59
SU-64	PBSU	150	89	0.302	6,400	15,500	2.44	40
SU-98		300	84	0.448	9,800	28,500	2.91	41
SU-169		500	92	0.597	16,900	55,300	3.27	36
SE-102	PBSE	300	90	0.380	10,200	20,700	2.02	28
SE-166		500	95	0.592	16,600	70,300	4.23	29
DO-114	PBDO	300	92	0.478	11,400	29,300	2.58	18
DO-192		500	96	0.674	19,200	78,300	4.08	13

^a Measured by a Ubbelohde viscometer in chloroform at 30°C.

^b Determined by gel permeation chromatography in chloroform at 30°C.

^c Determined by DSC at a heating rate of 10°C/min under N₂.

$$G_{1c} = \frac{K_{1c}^2(1 - \nu^2)}{E} \quad (2)$$

where P is the maximum load obtained from the fracture curve, B the thickness of the specimen, w the width of the specimen, ν the Poisson's ratio, taken as 0.35, and E the flexural modulus from three point bending test; and

$$Y = f(R) = \frac{(2 + R)(0.886 + 4.64R - 13.33R^2 + 14.72R^3 - 5.6R^4)}{(1 - R)^{3/2}} \quad (3)$$

where R is the a/w and a the crack length.

Table II Details of the Resin Formulations and Cure Conditions^a Used

Code	Polyester ^b	
	Type	M_n (g/mole)
EAD-43	PBAD	4,300
EAD-64		6,400
ESU-64	PBSU	6,400
ESU-98		9,800
ESU-169		16,900
ESE-102	PBSE	10,200
ESE-166		16,600
EDO-114	PBDO	11,400
EDO-192		19,200
UE	Unmodified	

^a Cure condition: 1 h/120°C, 4 h/180°C.

^b Polyester content: 10 wt %.

RESULTS AND DISCUSSION

Aromatic polyesters are effective modifiers for toughening of the epoxy resin system. All polyesters used in this study are soluble in the epoxy resin in the absence of solvents. The experimental results of the cured unmodified and the polyester-modified DGEBA/DDM resin systems, obtained by SEM, RDS, DSC, and the mechanical measurement, are presented below in terms of the monomer type, polyester concentration, and the molecular weight.

Morphologies of Modified Epoxy Resins

The morphologies of the cured unmodified and polyester-modified resins investigated by SEM, are shown in Figures 3–5. The fracture surfaces for different concentrations of the modifier are shown in Figure 3. The fracture surfaces of the unmodified resin and the modified resin with 5 wt % of AD-64 was smooth and featureless at a magnification of 10,000. However, in the samples containing 10 and 15 wt % of AD-64 the fracture surfaces showed irregular particles, and an increase in the particle sizes with increasing concentration of AD-64 from 10 to 15 wt %.

The SEM micrographs for cured epoxy resin systems modified with PBSU are shown in Figure 4. We could not observe any drastic change in morphology as the molecular weight of PBSU was increased. But their fracture surfaces were more rough compared to the unmodified resin, which might be due to the good compatibility of polyesters and epoxy resin.^{19,20}

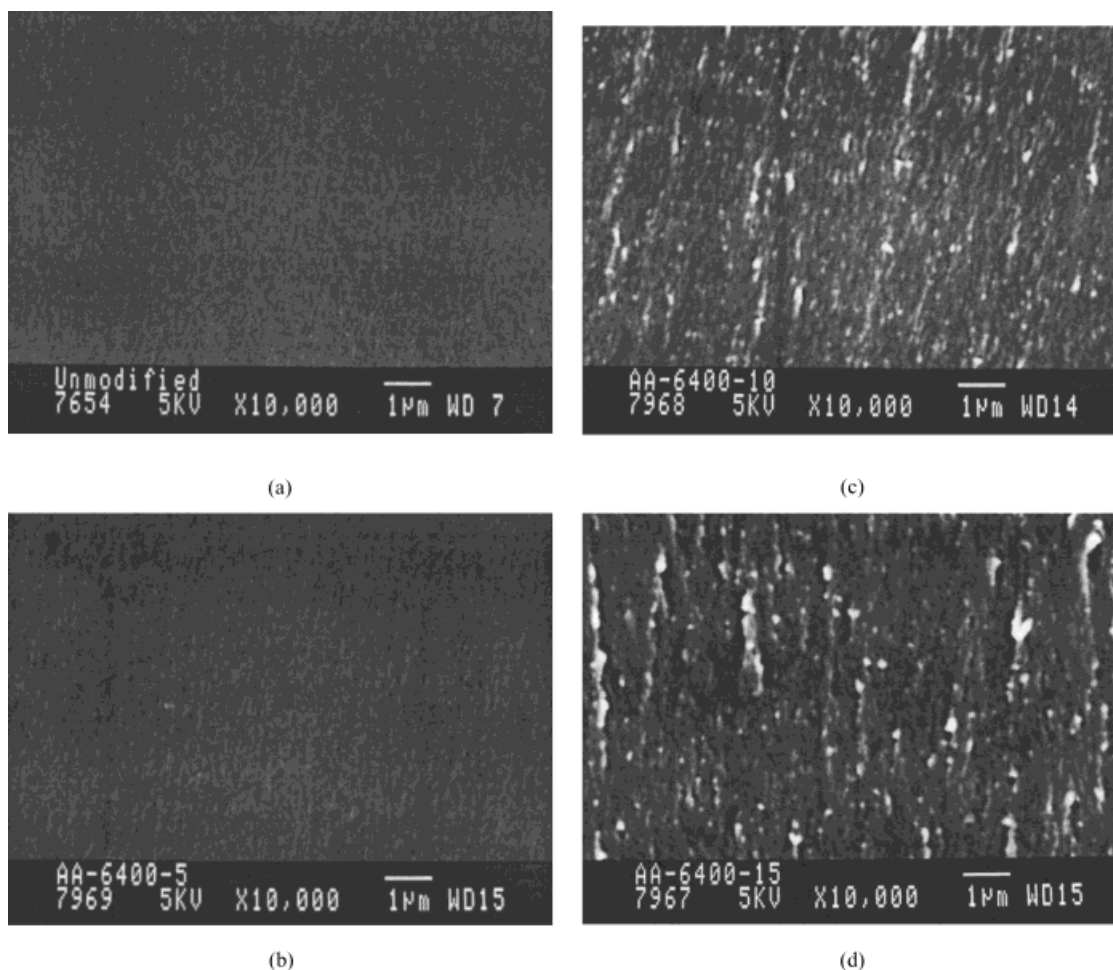


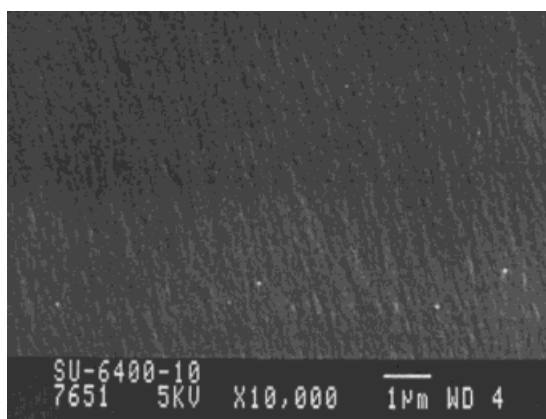
Figure 3 SEMs of fracture surfaces for cured epoxy resin systems modified with PBAD: (A) unmodified resin, (B) 5 wt %, (C) 10 wt %, and (D) 15 wt %.

The SEMs of the cured resins modified with different polyesters of alkylene chains are shown in Figure 5. In the epoxy resin modified with SU-98 and DO-114, the fracture surfaces were slightly rough and discrete particles were not observed. Meanwhile, the fracture surfaces for the epoxy resin modified with AD-64 and SE-102 was quite different from those for ESU-98 and EDO-114. The fracture surface for EAD-64 was a rough one, containing ridges and irregular particle. In ESE-102 system, spherical particles were observed with an average size of about 0.2 μm and a two-phase structure was conformed.

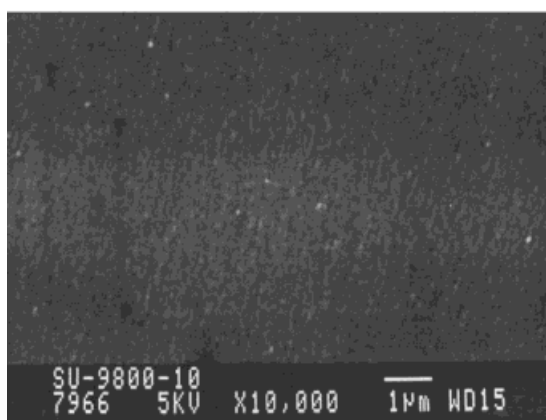
In the systems modified by SU-98 and DO-114 the similar morphology of the homogeneous phase was observed, while in the systems modified by AD-64 and SE-102 SEMs showed the microphase separated structure. These results are not clearly understood yet and further experimental work is being carried out in our laboratory.

Dynamic Viscoelastic Analysis of Modified Resins

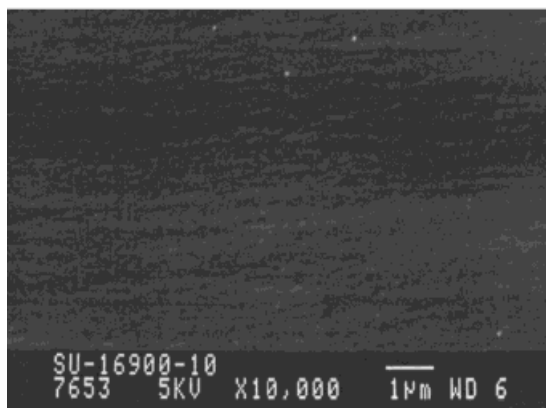
Dynamic viscoelastic analysis can give information on the microstructures of cured resins. The $\tan \delta$ curves for the unmodified resin and the polyester-modified resin system (ESU-98) are shown in Figure 6. The peak position of the α relaxation in the $\tan \delta$ curves shifted toward a lower temperature with increasing the polyester content. In this system α relaxation of the cured epoxy resin had lower values (170, 159, and 146°C) than that of the unmodified resin (183°C), which indicates that the epoxy resin is plasticized by polyester dissolved in the matrix. The β relaxation peak from the motion of hydroxyether group in the cured epoxy resin was observed at around -60°C . The effect of the polyester molecular weight on $\tan \delta$ was investigated in the cured resin modified with PBSU (Figure 7). The α relaxation temperatures was similar (159, 159, and



(a)



(b)



(c)

Figure 4 SEMs of fracture surfaces for cured epoxy resin systems modified with PBSU: (A) $M_n = 6400$ g/mole, (B) $M_n = 9800$ g/mole, and (C) $M_n = 16,900$ g/mole.

160°C) regardless of the difference in the molecular weight. But in the ESU-64 system, the α relaxation peak of the $\tan \delta$ curve was slightly broader than those of ESU-98 and ESU-169 systems.

The effect of the alkylene chain lengths on the $\tan \delta$ curves for the cured modified resin system is shown in Figure 8. Meanwhile, in the $\tan \delta$ curves, α relaxation peaks of EAD-64 and ESE-102 appeared at 174 and 178°C, and α' relaxation peaks were observed at 61 and 28°C. The existence of the α' relaxation peak indicates the existence of a phase-separated structure, which corresponds to the morphological observation [Figure 5(A),(C)]. The α' relaxation peak was not observed in the ESU-98 and EDO-114 systems.

Mechanical and Thermal Properties of Modified Epoxy Resins

The physical properties of the cured epoxy resins on addition of 10 wt % of the polyester with various molecular weights are shown in Table III. In the cured modified resin K_{1c} , G_{1c} , flexural modulus, and flexural strength were greater, while tensile strength and the glass transition temperature (T_g) showed smaller values, compared to those of unmodified resin. Both K_{1c} and G_{1c} increased with increasing the molecular weight. Especially, K_{1c} and G_{1c} in the EAD-64 and ESE-102 systems were greater than those of the other systems. This result is consistent with that of the T_g measurement.

DSC thermograms of the cured resin systems (ESU-98) modified with PBSU are shown in Figure 9. The T_g values were rapidly decreased with increasing the polyester concentration. As mentioned above, it is considered to be due to the plasticizing effect. However, in the ESE-102 system the decrease in T_g values was not significant with increasing the polyester concentration (Figure 10). It is believed to be due to the phase separated structures of the epoxy resin and polyesters,^{19,20} as seen from the morphology and the viscoelastic behaviors. DSC thermograms for the cured modified resin systems with different PBSU molecular weights are shown in Figure 11. The T_g values were similar regardless of the difference in the molecular weight.^{19,21} The effects of the polyester chain unit for cured modified resin systems are shown in Figure 12. Two T_g values were observed due to the phase separation in EAD-64 and ESE-102. The T_g values of EAD-64 and ESE-102 were greater than those of ESU-98 and EDO-114, which are miscible systems. And it is consistent with the result described in viscoelastic behavior.

The critical stress intensity factor K_{1c} is shown in Figures 13 and 14, as a function of the molecular weight, the concentration and the chain

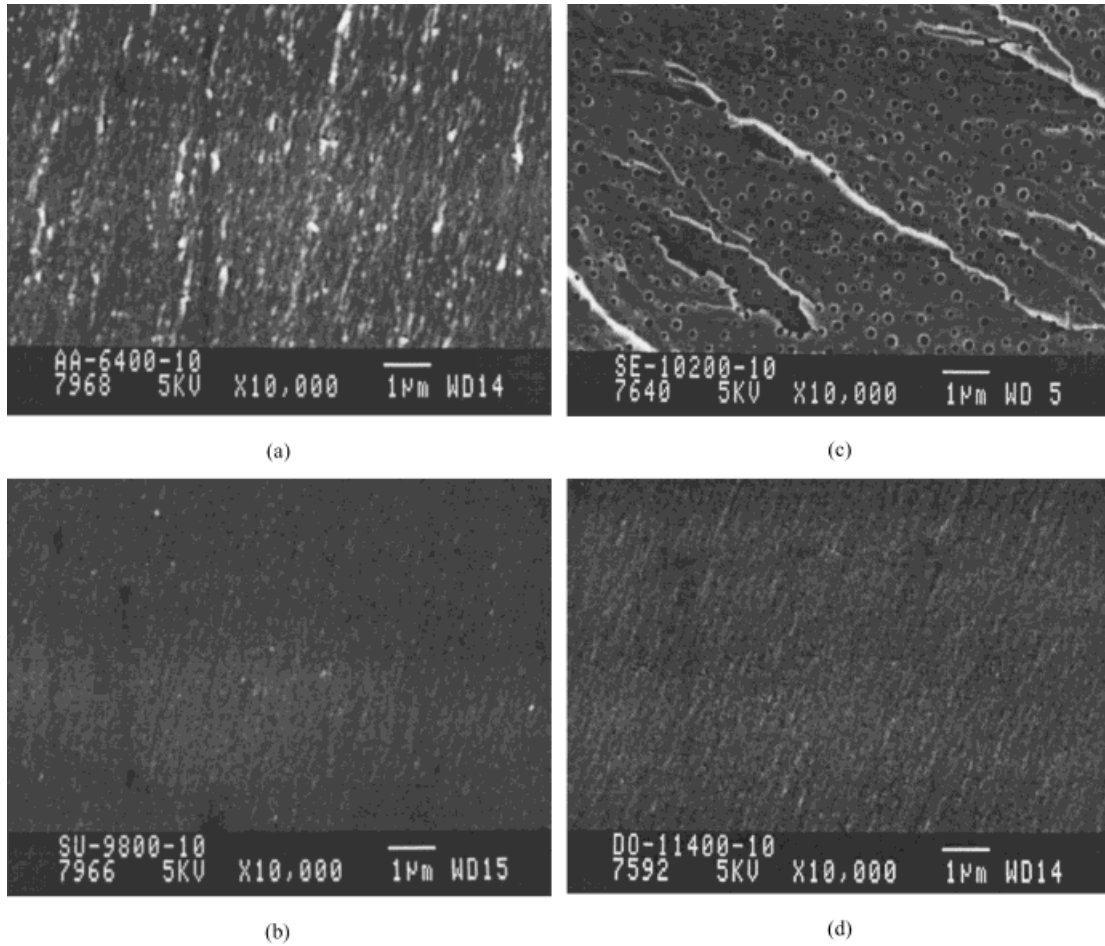


Figure 5 SEMs of fracture surfaces for cured epoxy resin systems modified with different polyesters: (A) EAD-64, (B) ESU-98, (C) ESE-102, and (D) EDO-114.

length unit of polyesters. The fracture toughness (K_{Ic}) of the resin system modified with 15 wt % of polyester did not change much with the molecular weight of polyester as shown in Figure 13. But the

fracture toughness of the resin systems modified with 5 and 10 wt % of polyester increased significantly with increasing the molecular weight. The

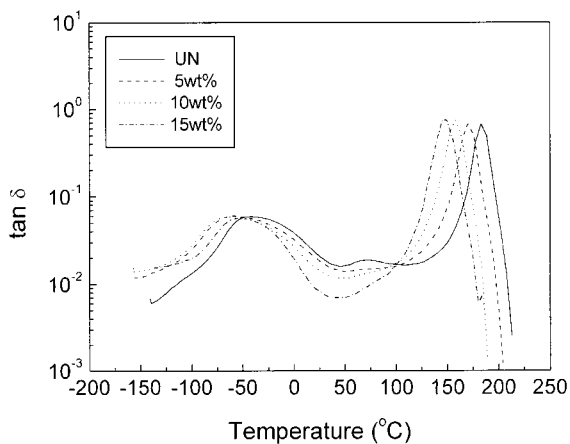


Figure 6 The effect of PBSU content on $\tan \delta$ for the ESU-98 (5, 10, 15 wt %).

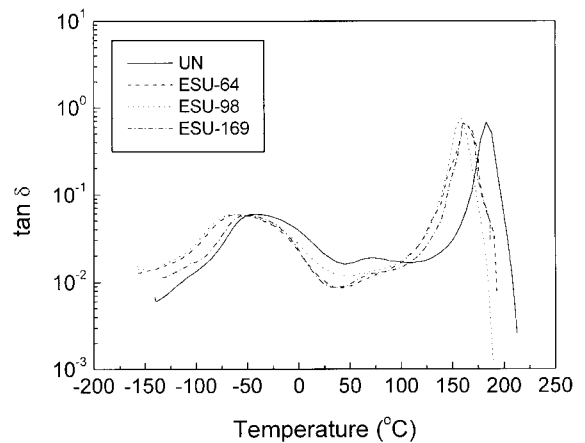


Figure 7 The effect of molecular weight of polyesters on $\tan \delta$ for cured resins modified with 10 wt % polyesters (ESU-64, ESU-98, ESU-169).

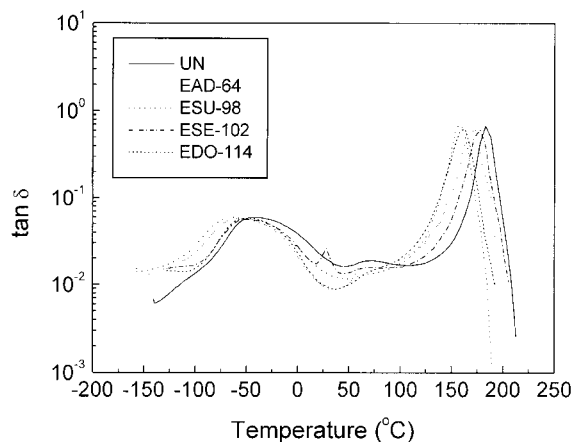


Figure 8 The effect of alkylene chain units of polyesters on $\tan \delta$ for cured resins modified with 10 wt % polyesters (EAD-64, ESU-98, ESE-102, and EDO-114).

maximum fracture toughness of the resin system modified with the high molecular weight polyester appeared at 10 wt %.^{22,23} The fracture toughness increased sharply in the region between 6400 and 9800 g/mole at 5 and 10 wt % of polyester concentration. Meanwhile, the fracture toughness of the resin system modified with a high molecular weight ($M_n = 16,900$ g/mole) polyester was almost similar to that of the system modified with the polyester of $M_n = 9800$ g/mole. The use of the 10 wt % polyester of $M_n = 9800$ g/mole led to a 30% increase in the K_{1c} value. With $M_n = 16,900$ g/mole, the similar K_{1c} value was observed. But the use of the 15 wt % of $M_n = 6400$, 9800, or 16,900 g/mole increased K_{1c} only

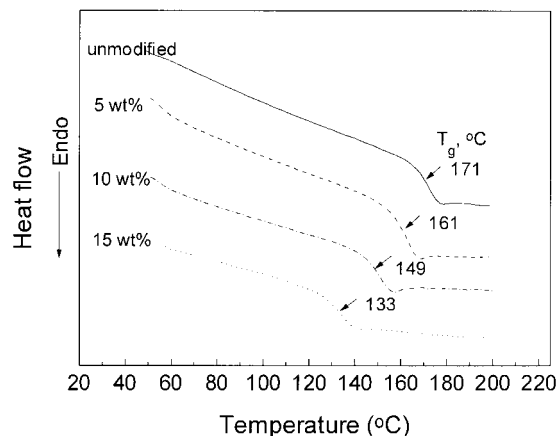


Figure 9 DSC thermograms of cured epoxy resins modified with PBSU ($M_n = 9800$ g/mole).

slightly, compared to the unmodified resin system.

The effects of the alkylene chain lengths of polyesters on the fracture toughness are shown in Figure 14. Iijima et al. reported that K_{1c} decreased with increasing the chain lengths of polyesters.¹⁹ In this system K_{1c} values did not change with the chain length of polyesters. EAD-64 system had high K_{1c} values, even though its molecular weight ($M_n = 6400$ g/mole) is low. The ESE-102 system showed a maximum K_{1c} at 10 wt % polyester content, 46% higher than the K_{1c} of the unmodified resin. This result agrees with that of SEM and dynamic mechanical measurements. The K_{1c} values of EDO-114 and EDO-192 systems (Table III) were similar to those of ESE-102 sys-

Table III Physical Properties of Modified Epoxy Resins

Code	Polyester ^a		K_{1c} (MN/m ^{3/2})	G_{1c} (J/m ²)	Flexural Modulus (kg/mm ²)	Flexural Strength (kg/cm ²)	Tensile Strength (kg/cm ²)	T_g^b (°C)
	Type	M_n (g/mole)						
Unmodified	—	—	0.77	195	264	879	720	171
EAD-43	PBAD	4,300	0.89	247	286	959	786	148
EAD-64		6,400	0.96	305	270	911	629	160
ESU-64	PBSU	6,400	0.85	245	288	1,024	678	149
ESU-98		9,800	0.99	335	268	876	589	149
ESU-169		16,900	1.02	304	266	874	532	151
ESE-102	PBSE	10,200	1.11	440	269	902	591	163
ESE-166		16,600	1.01	341	263	884	586	148
EDO-114	PBDO	11,400	0.95	303	264	887	725	148
EDO-192		19,200	1.02	352	263	931	615	144

^a Polyester content: 10 wt %.

^b Determined by DSC at a heating rate of 10°C/min.

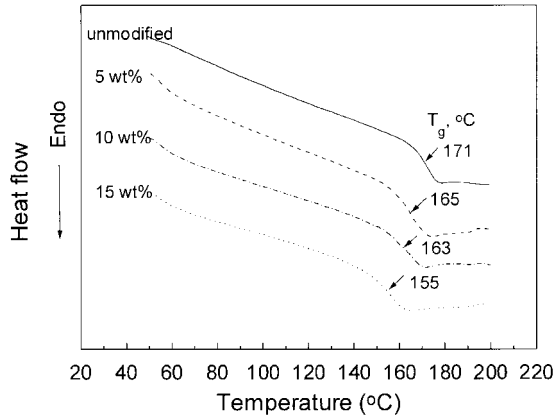


Figure 10 DSC thermograms of cured epoxy resins modified with PBSE ($M_n = 10,200$ g/mole).

tem, but T_g decreased rapidly. ESU-169 system revealed a 34% increase in the K_{1c} value with no expense of the flexural properties but its T_g decreased. Meanwhile, EAD-64 and ESE-102 systems showed interesting results, where the K_{1c} values increased by 26 and 46% with a slight expense of T_g (Table III, Figure 14). The T_g values of the modified resin systems (Table III) were much lower than that of the unmodified resin system. It is believed that the polyesters dissolve in the epoxy matrix. However, in the EAD-64 and ESE-102 systems the T_g values were higher than the other systems. SEM observation and dynamic viscoelastic measurements yielded the same results.

The flexural moduli of the polyester-modified resin systems, which were obtained in the three-point bending test, are shown in Figures 15 and

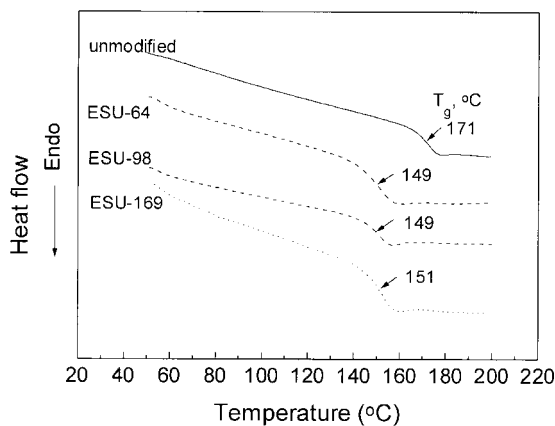


Figure 11 DSC thermograms for cured epoxy resins modified with different PBSU molecular weight (PBSU content: 10 wt %).

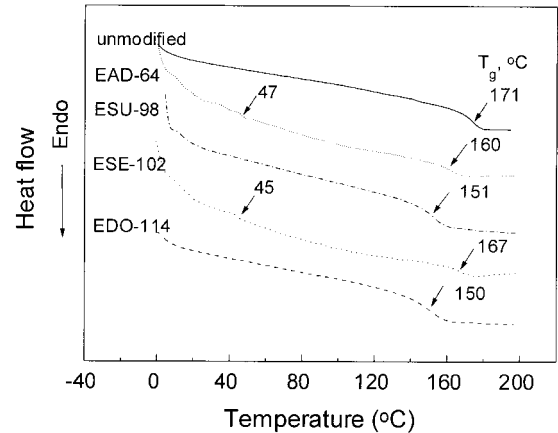


Figure 12 DSC thermograms for cured epoxy resins modified with different alkylene chain units of polyester (polyester content: 10 wt %).

16. The main drawback of the rubber modification is the significant reduction in the modulus of epoxy resin. However, the modification by polyester increases the flexural modulus of the epoxy resin within the range of the polyester concentration and the molecular weight employed in this study. Meanwhile, the flexural moduli of the modified resin systems decreased with increasing the polyester concentration and molecular weight. The flexural modulus of ESU systems showed a maximum at 5 wt % polyester. Iijima et al. also reported the similar trends in the epoxy systems with poly(butylene phthalate)s.²⁰ The transition phenomena of the polyester-modified systems containing 5 and 10 wt % polyester ($M_n = 6400$ g/mole) were not clearly understood. However, it

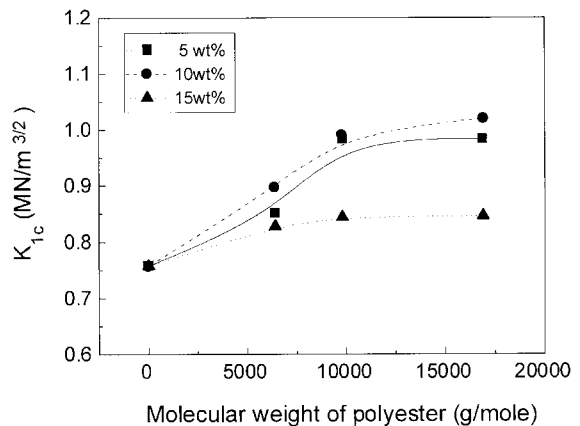


Figure 13 Plot of critical stress intensity factor K_{1c} against polyester molecular weight for cured epoxy resin systems modified with PBSU (5, 10, 15 wt %).

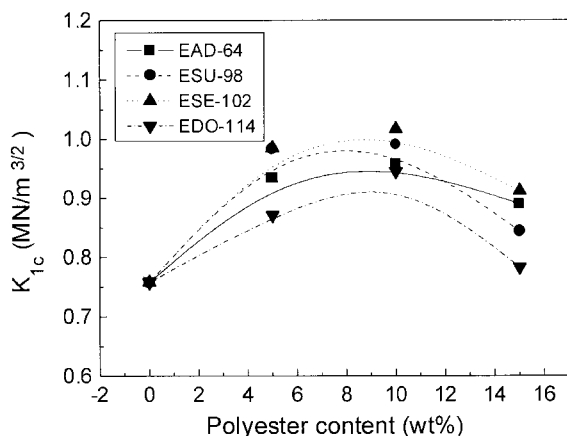


Figure 14 Plot of critical stress intensity factor K_{1c} against polyester content for cured epoxy resin systems modified with PBAD ($M_n = 6400$ g/mole), PBSU ($M_n = 9800$ g/mole), PBSE ($M_n = 10,200$ g/mole), and PBDO ($M_n = 11,400$ g/mole).

was believed to be due to the complex contribution of the stiffness of the epoxy network and of polyester to the modulus of the system. The flexural moduli of the modified resin systems decreased with increasing the alkylene chain units of polyesters.

The toughening mechanism can be explained in terms of the morphological and the dynamic viscoelastic behaviors. It is well known that epoxy resins can be toughened by the modification with reactive liquid rubbers or reactive acrylic elastomers.^{24–26} The elastomer particles having a diameter of a few microns are dispersed in the epoxy matrix. The toughening with elastomers is achieved by two mechanisms: one is the shear

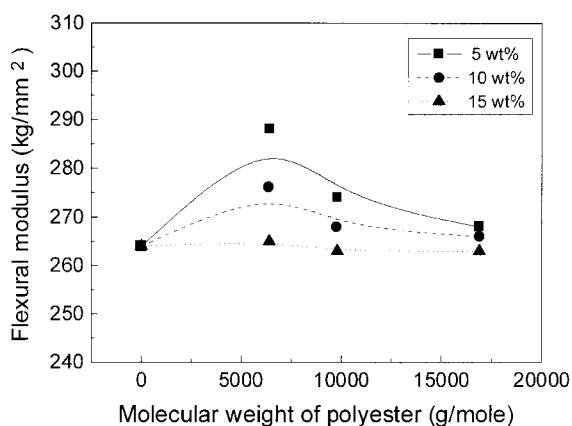


Figure 15 Plot of flexural modulus against polyester molecular weight for cured epoxy resin systems modified with PBSU (5, 10, 15 wt %).

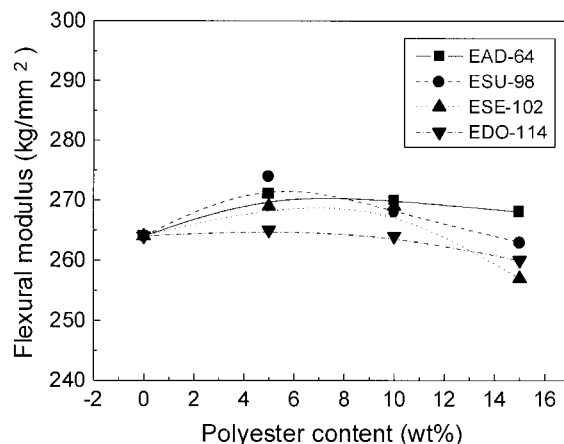


Figure 16 Plot of flexural modulus against polyester content for cured epoxy resin systems modified with PBAD ($M_n = 6400$ g/mole), PBSU ($M_n = 9800$ g/mole), PBSE ($M_n = 10,200$ g/mole), and PBDO ($M_n = 11,400$ g/mol).

band formation of the matrix near the crack based on the deformation of the dispersed particles as stress concentrators and the other is the particle elongation and tearing during the crack propagation with crack deflection and bifurcation.^{26–28}

The toughening of epoxy resins modified with polyesters would be achieved by the particulate structure. There are a couple of factors of importance in improving the brittleness of epoxy resins: the reinforcement of the matrix itself because of the incorporation of fine polyester-rich particles (<1 μm diameter), and the existence of the new relaxation.^{19,20} The existence of the α' relaxation near room temperature is one of the most important factors to reduce the brittleness of epoxy resins in EAD-64 and ESE-102 systems. Such behavior leads to the increase of the K_{1c} . It was reported that the presence of the relaxation peak near room temperature was effective in improving the toughness of the epoxy resin because of the increase in the area of the plastic deformation zone which was in turn attributed to the increase in temperature at the crack front.²⁹

The morphological and dynamic viscoelastic behavior of the EAD-64 and ESE-102 systems indicate that the microphase separation is important in reducing the brittleness of the epoxy resin, where the delocalized plastic deformation around particles dissipates the fracture energy. The increased K_{1c} value in the ESE-102 system suggests that the toughening of the epoxy matrix itself would be also important in improving the toughness of the epoxy resin.

CONCLUSION

Aromatic polyesters were found to be effective as modifiers for the epoxy resin. Their effectiveness depended on the polyester structure, the molecular weight and the concentration of polyester in the epoxy resin. The toughening in the modified epoxy resins might result from the phase-separated structures, as seen in the EAD-64 and ESE-102 systems. The most suitable compositions for the toughening was 10 wt % of SE-102, which resulted in a 46% increase in the fracture toughness, K_{1c} without a sacrifice in flexural properties. However, its thermostability became slightly worse, compared to the unmodified resin system. The use of higher molecular weight polyesters led to a decrease in mechanical properties of the cured resins owing to the macrophase separation.

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