

Preparation of Epoxy-Terminated Poly(Aryl Ether Sulfone)s and Their Use as Modifiers for Epoxy Resins

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SYNOPSIS

Epoxy-terminated poly(aryl ether sulfone)s (PSE) were prepared by the reaction of epichlorohydrin with hydroxyethyl-terminated polysulfones, which were synthesized from chloro-terminated polysulfones (PSC) and diethanolamine. Both PSE and PSC were used as modifiers for toughening of bisphenol A diglycidyl ether epoxy resin cured with *p,p'*-diaminodiphenyl sulfone. The mechanical, thermal, and dynamic viscoelastic properties of the modified resins were examined and compared to the parent epoxy resin. The effectiveness of PSC was larger than that of PSE. The fracture toughness, K_{IC} , for the modified resin increased 45% at slight expense of its mechanical properties on 20 wt % addition of PSC (M_w 5300). These results were discussed in terms of the morphological and dynamic viscoelastic behaviors of the modified epoxy resin system.

INTRODUCTION

Epoxy resins are one of the most important thermosetting polymers and have wide use as structural adhesives and matrix resins for fiber composites, but their cured resins have one drawback; they are brittle and have poor resistance to crack propagation. The toughness of epoxy resins has been increased by blending with reactive liquid rubbers such as carboxyl-terminated butadiene acrylonitrile rubbers (CTBN).¹ The incorporation of CTBN tended to decrease glass transition temperatures, T_g 's, of modified resins. In previous studies epoxide-containing acrylic rubbers, prepared by copolymerization of *n*-butyl acrylate (BA) with vinylbenzyl glycidyl ether (VBGE)^{2a} or terpolymerization of BA, VBGE and styrene (St) or acrylonitrile (AN),^{2b} have been reported as decreasing the brittleness of epoxy resins. The use of reactive butyl acrylate rubbers reduces the expense of mechanical properties of modified resins to some extent.

Engineering thermoplastics are interesting materials as modifiers for epoxy resins from the view-

point of the maintenance of mechanical and thermal properties for the matrix resins. Modifications of epoxy resins with various types of ductile thermoplastics have been studied as an alternative to reactive rubber toughening for improving the toughness of epoxy resins. Recent studies have focused on modification of epoxy resins with poly(ether sulfone)s (PES). At first commercial poly(ether sulfone)s such as Vitrex were used as modifiers,³ but were less effective owing to poor interfacial bonding between two uncompatibilized phase in the cured resin.⁴ Terminally functionalized polysulfones are more effective modifiers than commercial PES. Hedrick et al. has modified a bisphenol-A-type epoxy resins using phenolic hydroxyl-terminated PES oligomers, where the fracture toughness, K_{IC} , increased 100% in the modification with PES (M_n 8200).⁵ Both amine- and hydroxy-terminated PES were also effective modifiers.^{6,7} Most recently, other engineering thermoplastics have been examined as modifiers. Poly(aryl ether ketone)s were used as modifiers in the modest increase in the K_{IC} values.⁸ Polyetherimide⁹ and poly(phenylene oxide)¹⁰ have been reported as effective modifiers. Aromatic polyester, prepared by the reaction of phthalic or isophthalic acids and α,ω -alkanediols, were interesting materials as modifiers.¹¹ The aromatic polyesters

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were soluble in bisphenol-A-type epoxy resins without using solvents and effective modifiers for the epoxy resins. For example, the incorporation of 20 wt % of poly(ethylene phthalate) (M_w 7200) resulted in a 150% increase in the K_{IC} value at no expense of mechanical properties of methyl hexahydrophthalic anhydride-cured epoxy resins.

This work reports the preparation and use as modifiers of epoxy-terminated poly(ether sulfone)s for the *p,p'*-diaminodiphenyl sulfone-cured epoxy resins (diglycidyl ether of bisphenol A). Epoxy-terminated PES has not been found in the literature. The effect of the amount and composition of added PES on the mechanical properties of the cured epoxy resin was examined.

EXPERIMENTAL

Materials

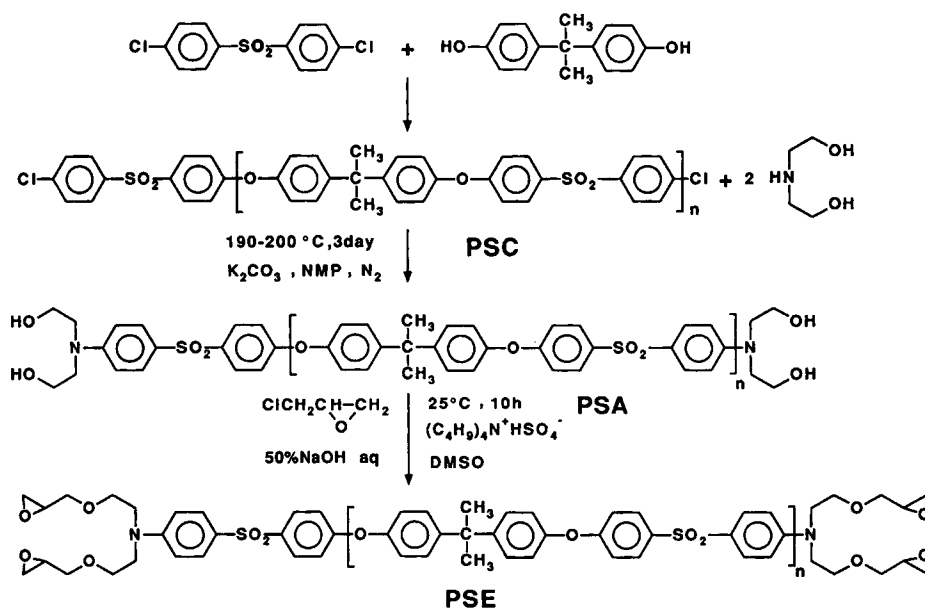
p,p'-Dichlorodiphenyl sulfone (Nissan Chemical Industry Co.) was recrystallized three times from toluene, mp 149–150°C. Bisphenol A was recrystallized three times from 20 wt % aqueous acetic acid, mp 156–159°C. The epoxy resin used was the liquid bisphenol-A-type epoxy resin (DGEBA) [AER 331, Asahi Chemical Industry Co., epoxy equivalent weight (EEW) 191]. *p,p'*-Diaminodiphenyl sulfone (DDS) was used as a curing agent. Solvents such as toluene and *N*-methyl pyrrolidone (NMP) were purified in the usual way. Other reagents were used as received.

Measurements

Molecular weights of polysulfones were determined by gel permeation chromatography (Shimadzu LC-5A instrument) using polystyrene standards. IR spectra were obtained on Shimadzu FT-IR-4000 type. $^1\text{H-NMR}$ spectra were measured on a 90 MHz instrument (JEOL JNX-FX 90) using CDCl_3 as a solvent. Epoxy groups in polymers were determined by the HCl dioxane method.¹² Hydroxyl groups in polymers were analyzed by acetylation.¹³ Glass transition temperatures of both polysulfones and cured resins were measured by differential scanning calorimetry (Shimadzu DSC 41M type). Mechanical properties of cured resins were determined with a Shimadzu autograph AGS-500B universal testing machine. Flexural tests were carried out at a crosshead speed of 2 mm/min (JIS K7203). Fracture toughness, K_{IC} , was measured in a three-bent geometry at a crosshead speed of 1 mm/min (ASTM E-399). Scanning electron micrographs were taken with a JEOL JSM instrument using failed specimens in the K_{IC} tests. Dynamic viscoelastic analysis was performed with a Rheometrics RDS-II type (Rheometrics Co.) between –150 and 250°C at a heating speed of 5°C/min at frequency of 1 Hz.

Preparation of Epoxy-terminated Poly(Aryl Ether Sulfone)s

Epoxy-terminated PES was prepared via hydroxyethylation of chloro-terminated PES (Scheme 1).



Scheme 1

Table I Characterization of Chloro-terminated Poly(aryl ether sulfone)s

Entry No.	M_n^a	M_w^a	M_{GPC}^a	M_w/M_n^a	T_g (°C) ^b
PSC 1	2,800	4,800	4,500	1.70	—
PSC 2	2,700	4,600	4,400	1.68	—
PSC 3	3,000	5,300	4,900	1.77	128
PSC 4	6,500	20,700	24,700	3.17	163
PSC 5	15,600	69,200	76,400	4.42	180

^a By gel permeation chromatography (GPC).

^b By differential scanning calorimetry (DSC).

Table II Hydroxyethylation of Chloro-terminated Polysulfones

Entry No.	PSC		DA ^b g (mol)	Yield (%)	PSE			H.E.W. (g/eq) ^d
	No. ^a	wt (g)			M_n^c	M_w^c	M_w/M_n^c	
PSA 1	PSC 1	150	140 (1.33)	91	2,700	4,300	1.59	764
PSA 2	PSC 2	200	256 (2.43)	81	3,100	4,300	1.42	815
PSA 3	PSC 4	170	147 (1.40)	98	3,800	7,800	2.04	1,210
PSA 4	PSC 5	170	78.9 (0.75)	92	5,800	14,800	2.57	2,310
PSA 5 ^e	PSC 5	5	2.0 (0.019)	—	3,900	7,400	1.91	—
PSA 6 ^f	PSC 5	5	2.0 (0.019)	—	4,000	7,300	1.85	—

^a Entry number in Table I.

^b Diethanolamine.

^c By GPC.

^d Terminal hydroxyl equivalent weight (H.E.W.) obtained by acetylation.

^e At 150°C for 3 h.

^f At 150°C for 3 h in the dark.

Table III Preparation and Characterization of Epoxy-terminated Polysulfones

Entry No.	PSA		ECH/ DMSO (g/g)	Time (h)	Yield (%)	PSE					
	No. ^a	wt (g)				M_n^b	M_w^b	M_w/M_n^b	EEW ^c	(Calcd) ^d	T_g (°C) ^e
PSE 1	PSA 1	10	100/0	5	81	3,600	6,000	1.64	1,560	(820)	—
PSE 2	PSA 1	20	100/10	5	92	3,300	5,200	1.56	1,030	(820)	—
PSE 3	PSA 1	20	100/10	7	97	3,300	5,200	1.56	883	(820)	—
PSE 4	PSA 1	20	100/10	10	68	3,300	5,100	1.56	875	(820)	112
PSE 5	PSA 2	150	750/113	10	82	3,000	4,300	1.42	969	(871)	115
PSE 6	PSA 3	150	750/113	12	74	4,700	8,900	1.89	1,710	(1,270)	143
PSE 7	PSA 4	140	800/105	10	78	7,100	16,600	2.33	2,450	(2,370)	151

^a Entry number in Table II.

^b By GPC.

^c Epoxy equivalent weight obtained by the HCl/dioxane method.

^d Based on the HEW values of PSA.

^e By DSC.

Table IV Mechanical and Thermal Properties of Epoxy Resins Modified with PES

Entry No. Composition (DGEBA/ PES)	Tensile				Flexural				T_g^b (°C)	
	Strength (kgf/mm ²)	Elonga- tion (%)	Modulus (kgf/mm ²)	n^a	Strength (kgf/mm ²)	Modulus (kgf/mm ²)	n^a	K_{IC} (MN/m ^{2/3})		
100/10	9.42 ± 0.63	8.5 ± 1.2	171 ± 4	8	16.7 ± 0.7	353 ± 18	6	0.70 ± 0.04	6	184
PSE 5 series										
90/10	9.49 ± 0.74	8.4 ± 1.6	181 ± 4	6	15.9 ± 0.9	360 ± 11	7	0.71 ± 0.04	5	176
80/20	9.58 ± 0.63	9.3 ± 1.4	179 ± 7	7	14.9 ± 1.2	347 ± 9	7	0.69 ± 0.05	7	165
60/40	—	—	—	—	—	—	—	0.72 ± 0.03	6	159
PSE 6 series										
90/10	8.64 ± 0.75	7.2 ± 0.8	171 ± 6	8	15.0 ± 1.7	357 ± 6	7	0.77 ± 0.06	7	176
80/20	8.85 ± 0.69	8.2 ± 1.4	166 ± 7	6	14.3 ± 0.9	351 ± 17	6	0.83 ± 0.04	6	169
PSE 7 series										
90/10	8.58 ± 0.96	10.0 ± 1.7	130 ± 5	6	14.9 ± 1.9	323 ± 14	6	0.85 ± 0.05	6	191
80/20	9.44 ± 0.50	10.9 ± 1.5	132 ± 4	6	15.4 ± 1.8	329 ± 16	5	0.83 ± 0.06	5	182

^a Specimen number.^b By DSC.

Chloro-terminated PES was prepared by the step-growth polymerization of bisphenol A and *p,p'*-dichlorodiphenyl sulfone according to the modified

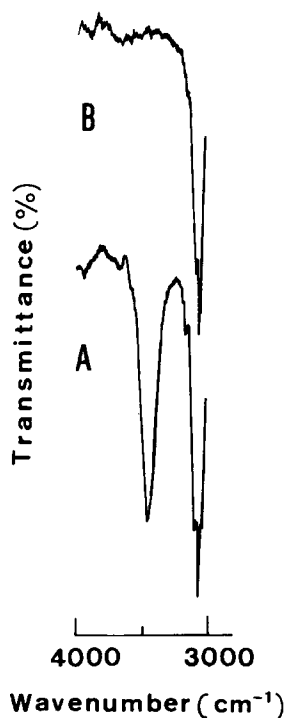
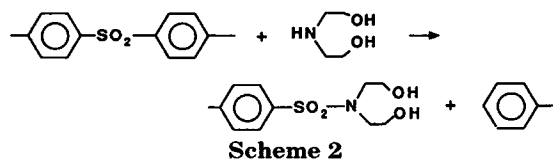


Figure 1 IR spectra of polysulfones. (a) Polysulfone prepared in the usual way; (b) chloro-terminated polysulfone (PSC).

method of Mohanty et al.¹⁴ Typical procedures are shown as follows.

First, 137.0 g (0.600 mol) of purified bisphenol A, 174.5 g (0.627 mol) of *p,p'*-dichlorodiphenyl sulfone, and 990 mL NMP were charged into a 2-L four-necked flask fitted with a mechanical stirrer, a Dean-Stark trap, a nitrogen inlet, and a thermometer. Then 87.1 g (0.630 mol) anhydrous potassium carbonate and 450 mL toluene were added. The flask was purged with N₂ and, a N₂ atmosphere was maintained throughout the polymerization. The reaction mixture was heated under reflux (to ca. 165°C) to remove water by azeotropic distillation. After water and toluene were removed from the reactor, the reaction mixture was stirred at 165–170°C for 10 h and then cooled to about room temperature. Further, 17.5 g (0.061 mol) *p,p'*-dichlorodiphenyl sulfone and 8.7 g (0.063 mol) K₂CO₃ was added and kept at 165–170°C for 5 h with stirring to make the terminal groups of PES chloride units quantitatively. The reaction mixture was then cooled, diluted with chlorobenzene, and filtered with a glass filter to remove the resulting inorganic salts. The filtrate was neutralized with acetic acid and diluted with tetrahy-



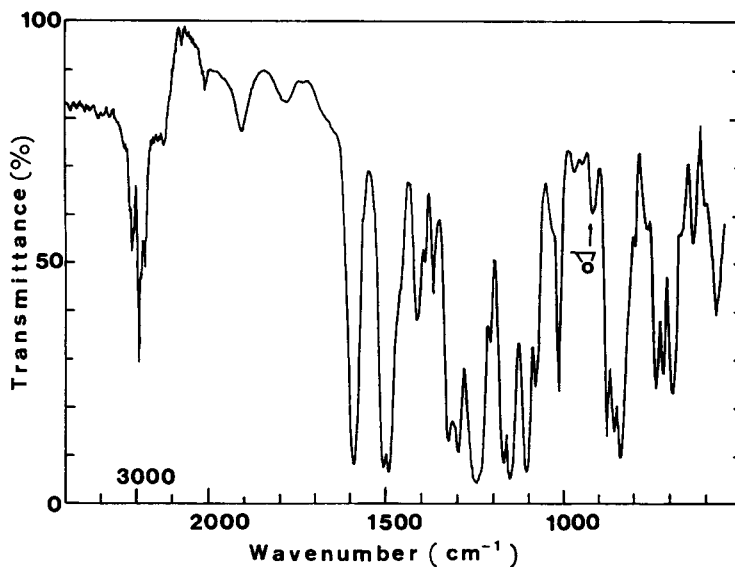


Figure 2 IR spectra of epoxy-terminated polysulfone (entry No. PSE 5).

dofuran (THF). Chloro-terminated PES was isolated using 50 vol % aqueous MeOH solution as a precipitant and purified by reprecipitation with THF-MeOH. PES was obtained in a quantitative yield after dried *in vacuo* at 80°C (entry No. PSC 2 in Table I).

Hydroxyl-terminated PES was prepared as reported previously.¹⁵ It is noteworthy that NMP was

used as a solvent. A typical procedure was briefly described.

A 1-L four-necked flask was charged with 200 g (Cl, 0.091 eq.) chloro-terminated PES (entry No. PSC-1 in Table I), 255.5 g (2.43 mol) diethanolamine, 6.9 g (0.05 mol) K₂CO₃, and 400 g NMP. The reaction mixture was kept at ca. 190°C for 3 h with stirring under N₂. After the reaction was over,

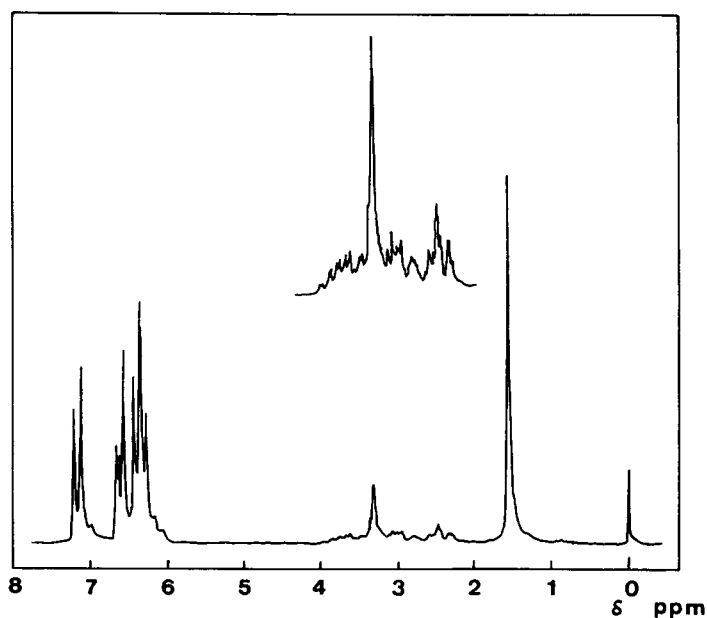


Figure 3 ¹H-NMR spectrum of epoxy-terminated polysulfone (entry No. PSE 5).

Table V Mechanical and Thermal Properties of the Modified Resin with PES

Entry No. Composition (DGEBA/PES)	Tensile			Flexural			T_g^b (°C)	n^a
	Strength (kgf/mm ²)	Elongation (%)	Modulus (kgf/mm ²)	Strength (kgf/mm ²)	Modulus (kgf/mm ²)	K_{IC} (MN/m ^{3/2})		
PSC 3 series								
90/10	9.82 ± 0.13	9.3 ± 0.9	179 ± 13	15.1 ± 0.7	339 ± 10	0.87 ± 0.07	184	4
80/20	8.94 ± 0.18	6.9 ± 0.1	185 ± 6	13.5 ± 1.2	335 ± 10	1.02 ± 0.05	132, 169	5
PSC 4 series								
90/10	9.52 ± 0.25	9.0 ± 0.8	179 ± 4	15.1 ± 1.0	328 ± 6	0.89 ± 0.04	181	5
80/20	—	—	—	—	—	0.90 ± 0.05	163, 187	4
PSC 5 series								
90/10	—	—	—	—	—	0.80 ± 0.04	174	5
Hybrid PES series (DGEBA/PSC 4/PSE 6)								
90/5/5	—	—	—	—	—	0.88 ± 0.06	—	7
80/15/5	—	—	—	—	—	0.81 ± 0.04	—	6
(DGEBA/PSC 5/PSE 6)								
90/5/5	—	—	—	—	—	0.79 ± 0.04	—	7

^a Specimen number.

^b By DSC.

the reaction mixture was filtered to remove organic salts and diluted with THF. PES was isolated by reprecipitation with 50% aqueous MeOH solution, filtered, and dried *in vacuo* at 80°C. Yield was 162 g (81%).

Epoxy-terminated PES was prepared under phase transfer catalyzed reaction conditions according to the modified method of the previous work^{15,16} as follows:

A four-necked flask was charged with 475 g (5.13 mol) epichlorohydrin (ECH), 236 g [NaOH 118 g (2.95 mol)] 50% aqueous NaOH solution, and 3.4 g (0.01 mol) tetrabutylammonium hydrogensulfate. Hydroxyl-terminated PES (entry No. PSA-1 in Table II) was added below 20°C under vigorous stirring over a period of 1 h. The reaction mixture was kept below 25°C for 10 h with stirring. After the reaction was over, the reaction mixture was poured into ice water and extracted with dichloromethane. The organic phase was neutralized by washing with aqueous NaCl-saturated solution, and the solvent was evaporated. The crude polymer was dissolved in THF, isolated using 50% aqueous MeOH solution as precipitant, and purified by reprecipitation with THF-MeOH and drying *in vacuo* at 70°C. Yield was 132 g (82%).

Curing Procedure

A mixture of the epoxy resin and PES was heated at 150°C to homogenize and degas. The curing agent, DDS, was added to the mixture, which was kept at 120°C to dissolve DDS. The resulting clean mixture was then poured into silicon mold preheated at 120°C. A curing cycle was 120°C for 1 h and 180°C for 5 h. The amount (wt %) of PES used was calculated based on the amount of the epoxy resin, DGEBA. The curing agent was used stoichiometrically to the total epoxy content of both the epoxy resin and PES.

RESULTS AND DISCUSSION

Preparation of Epoxy-terminated Poly(Aryl Ether Sulfone)s

Scheme 1 shows the preparation process of epoxy-terminated poly(aryl ether sulfone)s (PSE).

PES, prepared by the reaction of bisphenol A with a slight excess of *p,p'*-dichlorodiphenyl sulfone (DCDPS), contained terminal phenolic hydroxyl groups as shown in Figure 1(a). Further addition in a 10 mol % excess of DCDPS enabled us to prepare chloro-terminated PES (PSC), which was

shown by the disappearance of phenolic hydroxyl groups at 3450 cm^{-1} in Figure 1(b). Table I reports some characteristic properties of PSC. The glass transition temperature, T_g , increased with increasing the molecular weight of PSC.

Hydroxyethylation of PSC was carried out using diethanolamine in NMP as solvent (Table II). The molecular weights of the resulting hydroxyl-terminated PES (PSA) were lower than the starting PSC especially in the use of the higher molecular weight PSC. These unexpected results could not be explained fully. It has been reported that exposure to ultraviolet light resulted in substantial changes in the physical properties of PES such as intrinsic viscosity.¹⁷ The hydroxyethylation was carried out in the dark, but the difference in reaction behaviors was not observed (entry no. PSA 5 and 6 in Table II). This might be explained based on the scission of the main chain of PSC by diethanolamine, a nucleophile (Scheme 2).

Epoxydation of PSA was carried out under the phase transfer catalyzed reaction conditions as reported previously^{15,16} (Table III). Epoxydation proceeded at ca. 25°C for 10 h in the presence of DMSO as a solvent, where broad OH stretching vibration peaks at ca. 3600 cm^{-1} disappeared and an epoxy group absorption appeared at 915 cm^{-1} (Fig. 2). The signals of the glycidyl ether groups were also ob-

served in the region of ca. 2.1–4.0 ppm in the $^1\text{H-NMR}$ spectrum of PSE (entry No. PSE 5 in Table III), overlapped with those of oxyethylene units (Fig. 3). Epoxydation was slow in the absence of DMSO (entry No. PSE 1 in Table III). It is difficult to solve higher molecular weight PSA (entry No. PSA 4 in Table III) in the standard solvent composition, and ECH as solvent was used in a larger amount (Table III, entry No. PSE 7).

Mechanical and Thermal Properties of Epoxy Resins Modified with Poly(Aryl Ether Sulfone)s

Both PSE and PSC were used as modifiers for epoxy resins. Table IV shows the mechanical and thermal properties of the resins modified with PSE. The cured parent epoxy resin was transparent. The resins modified with PSE were also transparent. In the modification with PSE a decrease in tensile and flexural strength for the cured resins was not significant. The use of PSE 7 led to a slight decrease in tensile and flexural moduli for the modified resins. The K_{IC} values for the modified resins increased with an increase in the molecular weight of PSE used. On addition of 20 wt % of PSE 7 (M_w 16,600) the K_{IC} value increased 20%. The use of lower molecular weight PES such as PSE 5 (M_w 4300) brought about no increase in the K_{IC} values.

Table VI Morphological Results

Resin Composition DGEBA/PES	Feed Polymer ^a Weight Fraction	D^b	V_f^c	N^d
100/0	0	—	0	0
PSC 3 series				
90/10	0.077	0.3 ± 0.1	0.042	66.4
80/20	0.159	0.5 ± 0.1	0.256	140.5
PSC 4 series				
90/10	0.077	0.7 ± 0.2	0.170	39.5
80/20	0.159	1.1 ± 0.3	0.248	34.6
PSC 5 series				
90/10	0.077	0.9 ± 0.2	0.122	20.1
80/20	0.159	— ^e	— ^e	— ^e
Hybrid PES series (DGEBA/ PSC 4/PSE 6)				
90/5/5	0.078	0.5 ± 0.1	0.093	41.2
80/15/5	0.159	0.7 ± 0.2	0.249	64.1

^a Based on the total resin.

^b Average particle diameter in μm . The $\pm x$ values show standard deviations.

^c Volume fraction of dispersed particle.

^d Number of particle/100 μm^2 .

^e Not obtained owing to poor processability of uncured resin mixture.

Table V shows the results of the modification with PSC. The transparency of the resins modified with PSC tended to decrease with an increase in the molecular weight of the modifier, and the cured resin modified with the highest molecular weight PSC (entry No. PSC 5, M_w 69,200) became translucent. The addition of more than 10 wt % of PSC 5 made processing difficult owing to an increase in the viscosity of uncured sample mixtures. Tensile and flexural strength for the modified resins decreased slightly in the modification with 20 wt % of PSC 3. The K_{IC} values tended to decrease with increasing

the molecular weight of PSC used. Lower molecular weight PSC (entry No. PSC 3, M_w 5300) was a more effective modifier for the epoxy resin. On addition of 20 wt % of PSC 3 the K_{IC} value increased 45% at slight expense of its mechanical properties.

It has been reported that a commercial polysulfone such as Vitrex 100P (ICI, M_w 85,000) was not effective as modifiers for epoxy resins and that there was no increase in the fracture toughness of cured resins in spite of the existence of phase-separated structure. It is interesting that oligomeric PES, PSC 3 (M_w 5300), is more effective than higher molecular

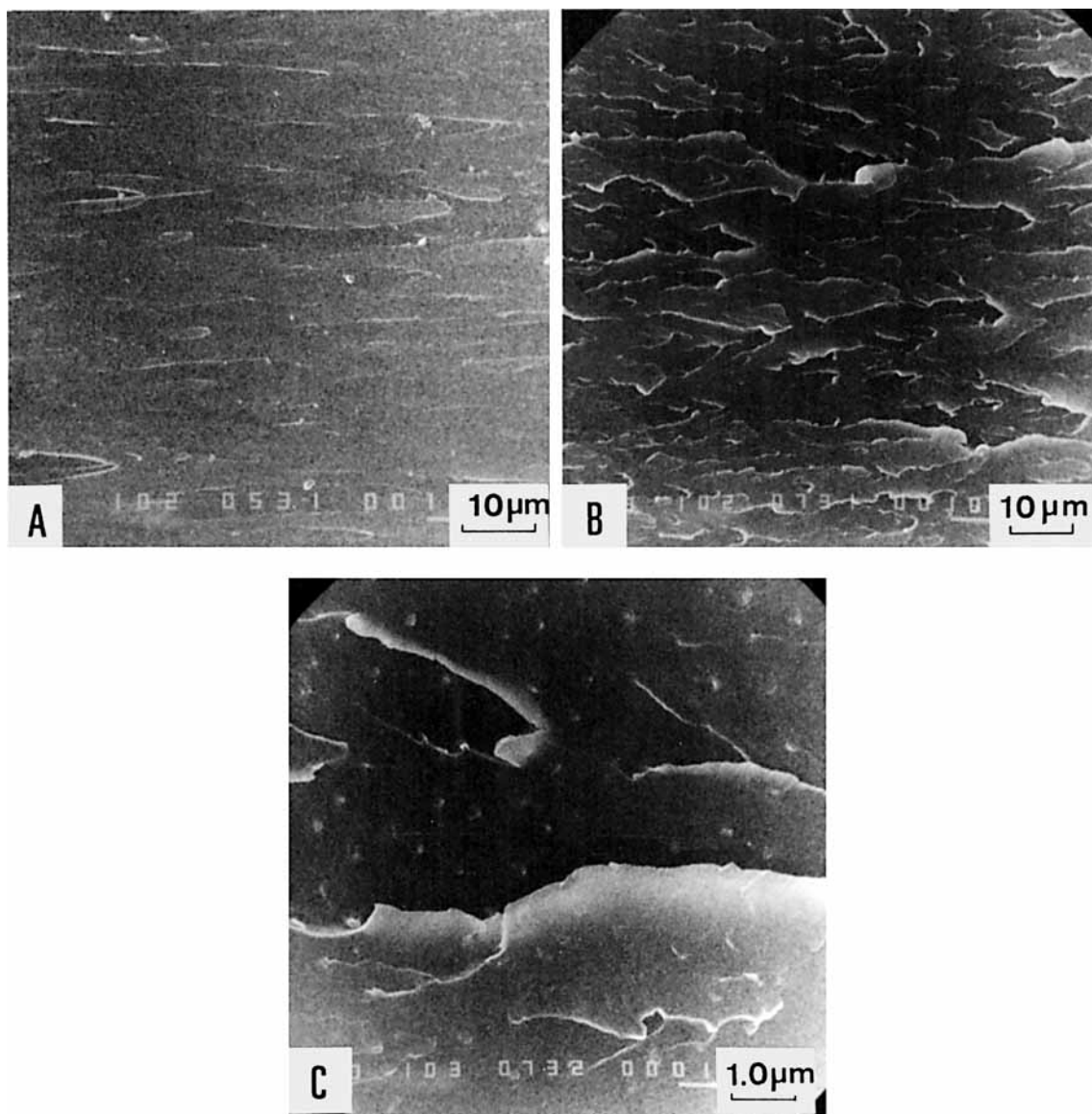


Figure 4 SEMs of fracture surfaces for the modified resins with 20 wt % of PSE. (a) PSE 6; (b) PSE 7, magnification 1000; (c) PSE 7, magnification 10000.

weight PES, considering that higher molecular weight polymers than 10,000 are more effective in the modification with terminally functionalized PES such as hydroxyl-terminated PES.⁷

These results show that PSC is a more effective modifier than PSE for the epoxy resin. This might be explained by the morphological behaviors of the modified resins as shown later. It is well-known that the two-phase structure and its interfacial bonding of the modified resin are important to decrease the brittleness of the epoxy resin in the modification with reactive rubbers.^{1,2} If the interfacial adhesion between PSC and the epoxy matrix would be strengthened, the effectiveness of PSC would enlarge to some extent. The use of PSE led to an improvement in the interfacial adhesion owing to covalent bonding between epoxy groups of PSE and the epoxy matrix. Based on such information, the mixtures of PSC and PSE were used as hybrid modifiers, but their effectiveness as modifiers was similar to that of PSC (Table V).

The modification with both lower molecular weight PSC 3 and PSE 5 resulted in a slight decrease in the glass transition temperatures, T_g , because of somewhat lower T_g of the polysulfones used. Two T_g 's were observed in the modification with 10 wt % of both PSC 3 and PSC 4. It is concluded that the lower T_g values (132 and 163°C) would be based on the polysulfone-rich phase and that the higher ones (169 and 187°C) on epoxy-rich matrix, from DSC results of the cured parent epoxy resin and polysulfones, morphologies of the modified resins (Fig. 5) and their dynamic viscoelastic behaviors (Fig. 8).

Morphology of the Modified Resins

The fracture surfaces of the cured resins were analyzed with the scanning electron microscope (SEM). Table VI shows morphological data for the cured resins. Figure 4 shows SEMs of the fracture surface of the PSE-modified resins. The unmodified resin had only one phase, and the fracture surface was smooth and featureless as reported previously.² The fracture surface for the resin modified with PSE 5 (M_w 4300) was also smooth and featureless even on addition of 60 wt % of the modifier: the surface was very similar to that for the parent epoxy resin. The fracture surface for the PSE 6 (M_w 8900) modified resin was rough and ridgy based on the plastic deformation of the epoxy matrix itself prior to failure [Fig. 4(a)], and there was a small amount of undefined particles less than 0.5 μm in the higher mag-

nification (X 10,000). In the modification with higher molecular weight PSE 7 (M_w 16,600) the fracture surface was also rough, containing ridges [Fig. 4(b)], and the existence of somewhat undefined particles less than 0.5 μm was observed at the magnification of 10,000 [Fig. 4(c)]. These results show that there is a high compatibility between PSE and the cured epoxy resin owing to interfacial covalent bonding. These morphological behaviors correspond to the effectiveness of PSE as modifiers. The morphology of the resin modified with PSE 7

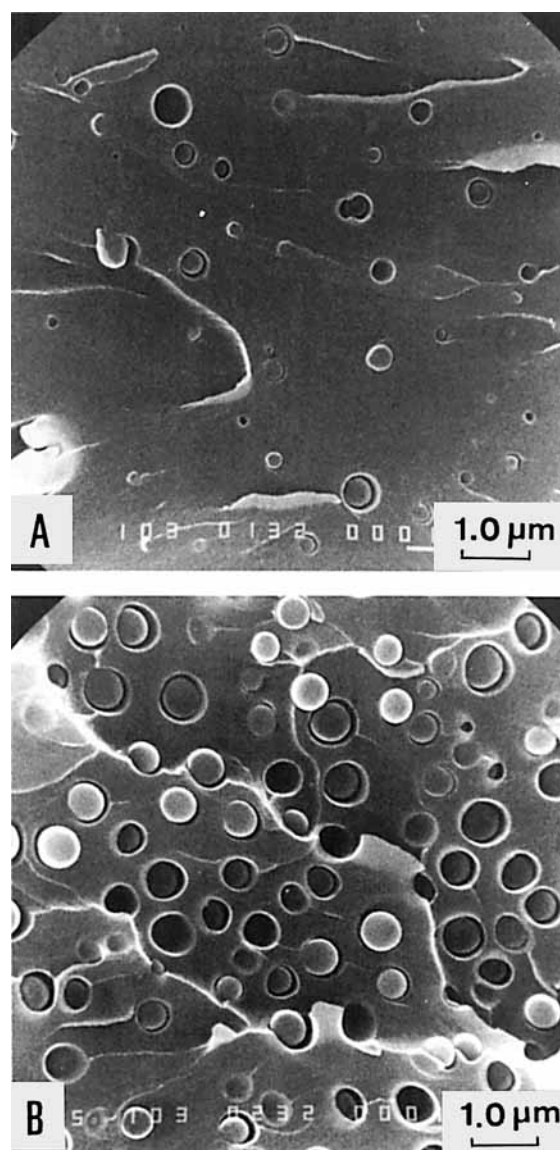


Figure 5 SEMs of fracture surfaces for the modified resins with PSC 3. (a) 10 wt % addition; (b) 20 wt % addition.

suggests that the molecular weight of PSE used in this study would not be satisfactory to result in the phase-separated structure perhaps owing to the high compatibility with the epoxy matrix and that PSE of molecular weight more than 17,000 would be more effective.

Figure 5 shows SEMs of fracture surfaces of the PSC-modified resins. The modified resins had two phase morphologies, but were transparent perhaps owing to similarity in the refractive index between

PSC and the epoxy matrix. On addition of 10 wt % of PSC 3 (M_w 5300) the volume fraction, V_f , of the dispersed particles was far smaller than the weight fraction of PSC 3 used. The morphology of the modified resin with 20 wt % of PSC 3 changed drastically; the volume fraction became far larger than the weight fraction of PSC 3 and both the particle diameter, D , and the number of particles, N , increased twice [Fig. 5(a) and 5(b)]. These morphological behaviors correspond to the results by dynamic vis-

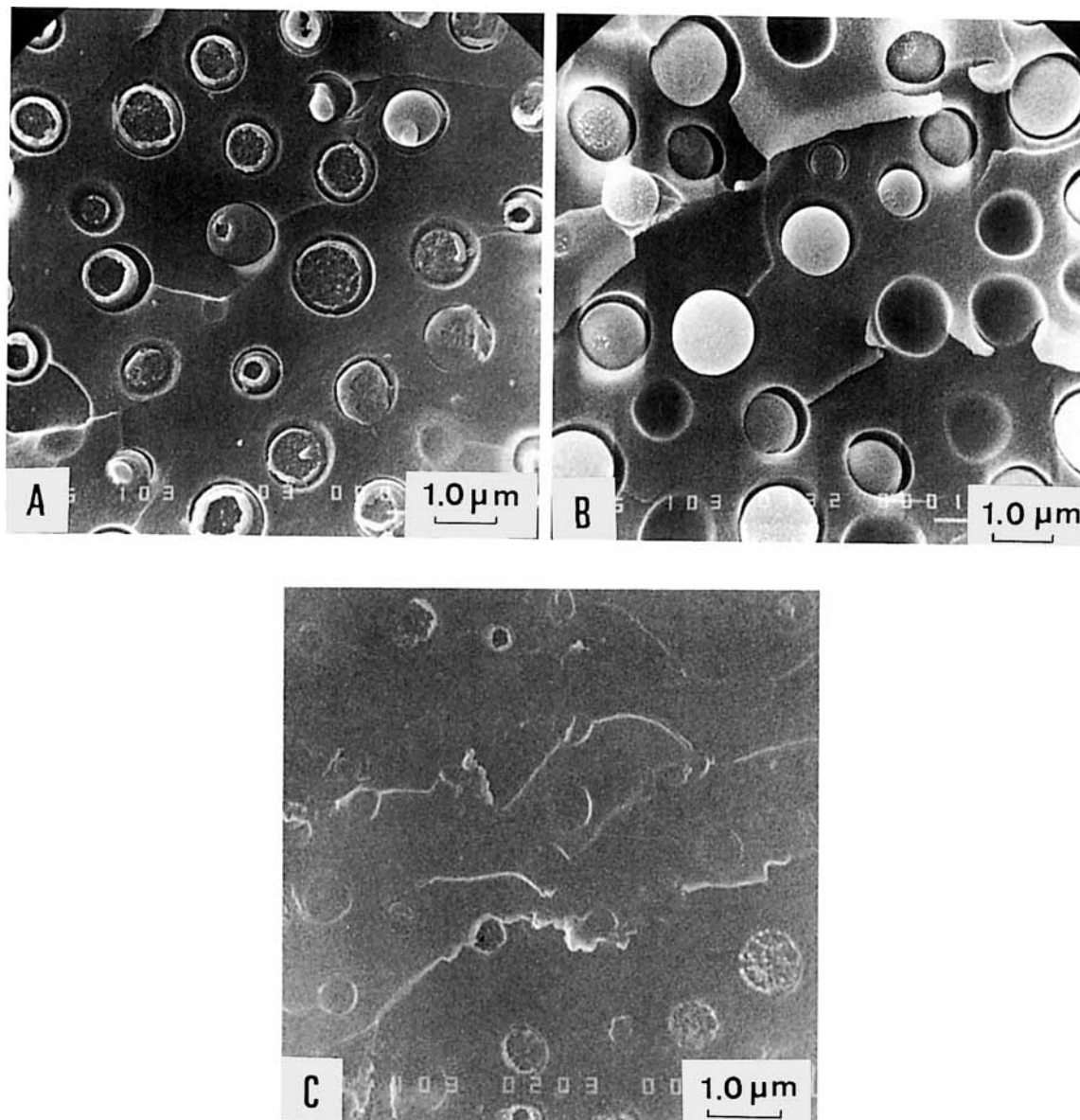


Figure 6 SEMs of fracture surfaces for the modified resins. (a) PSC 4, 20 wt %, in the initial stage; (b) PSC 4, 20 wt %, in the final stage; (c) hybrid PES (PSC 4, 15 wt % and PSE 6, 5 wt %).

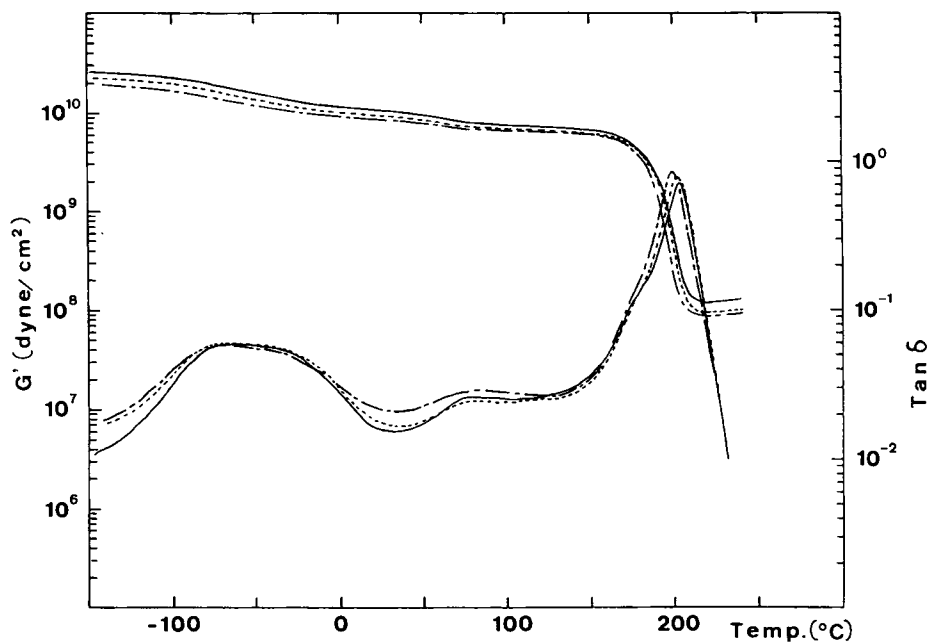


Figure 7 Dynamic viscoelastic analysis for PSE-6-modified cured resin. (—) control; (.....) 10 wt % addition; (---) 20 wt % addition.

coelastic analysis (shown later). These behaviors might explain the effectiveness of PSC 3 as a modifier. In the modification with PSC 4 (M_w 20,700)

the diameter and the volume fraction of the particles increased with an increase in the PSC 4 concentration, where the volume fraction of the dispersed

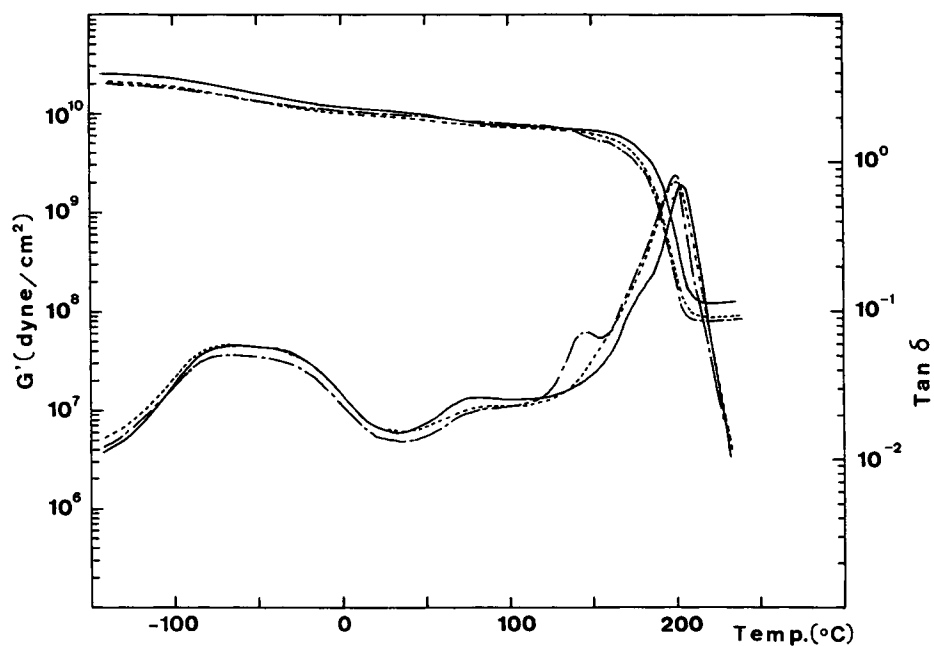


Figure 8 Dynamic viscoelastic analysis for PSC-3-modified cured resin. (—) control; (.....) 10 wt % addition; (---) 20 wt % addition.

particles were far larger than the weight fraction of PSC 4 used. This indicates that the dispersed particles contain the epoxy resin to some extent. The compatibility of the polysulfone with the epoxy matrix would be high, perhaps owing to similarity in the chemical structure between the polysulfones and the DDS-cured DGEBA-type epoxy resin system.

Morphologies of the resins modified with PSC are interesting and it is instructive to consider the toughening mechanism. They show that the particles dispersed in the epoxy matrix were torn in the initial stage of crack propagation but detached in the interface from the epoxy matrix, compared to the morphology of the modified resin in the fast propagation of crack [Fig. 6(a) and 6(b)]. This indicates that there are some interfacial adhesions between the epoxy matrix and PSC based on physical interactions such as the van der Waals forces. If the internal binding would become stronger owing to covalent bonding between polysulfones and the epoxy matrix, the effectiveness as modifiers might increase to some extent. The morphology of the resin modified with hybrid PES (PSC 4, 15 wt %, and PSE 6, 5 wt %) shows that there is no detachment in the interface in the initial stage of failure [Fig. 6(c)]. In spite of such an improvement in the interfacial adhesion, the effectiveness of the modifier does not appear unexpectedly. These results might be due to the low molecular weight of PES used.

Dynamic Viscoelastic Analysis of the Modified Resins

Dynamic viscoelastic properties can give information on the microstructure of cured resins. Figure 7 shows the results by dynamic viscoelastic analysis for PSE-6-modified resins. The peak position of the α -relaxation in the $\tan \delta$ curve shifted gradually toward lower temperature with increasing the content of PSE 6, but no new relaxation peak emerged and no tendency to phase separate was observed. The storage modulus decreased slightly with an increase in the modifier content. The magnitude at ca. 25°C in the $\tan \delta$ curve increased when the modifier content increased. This corresponds to the effectiveness of PSE 6 as a modifier. Such a correlation of low-temperature relaxation height (or area) with the toughness of the modified resin has been reported in the modification of epoxy resins with CTBN¹⁸ or reactive acrylic elastomers.^{2b}

In the modification with 10 wt % of PSC 3 the α -relaxation peak in the $\tan \delta$ curve became broader than that for the parent epoxy-cured resin, and the peak position of the α -relaxation peak for the former shifted slightly toward lower temperature, compared to that for the latter (Fig. 8). On 20 wt % addition of the modifier a new relaxation peak emerged at ca. 145°C in the $\tan \delta$ curve. This result indicates the existence of the phase-separated structure for the

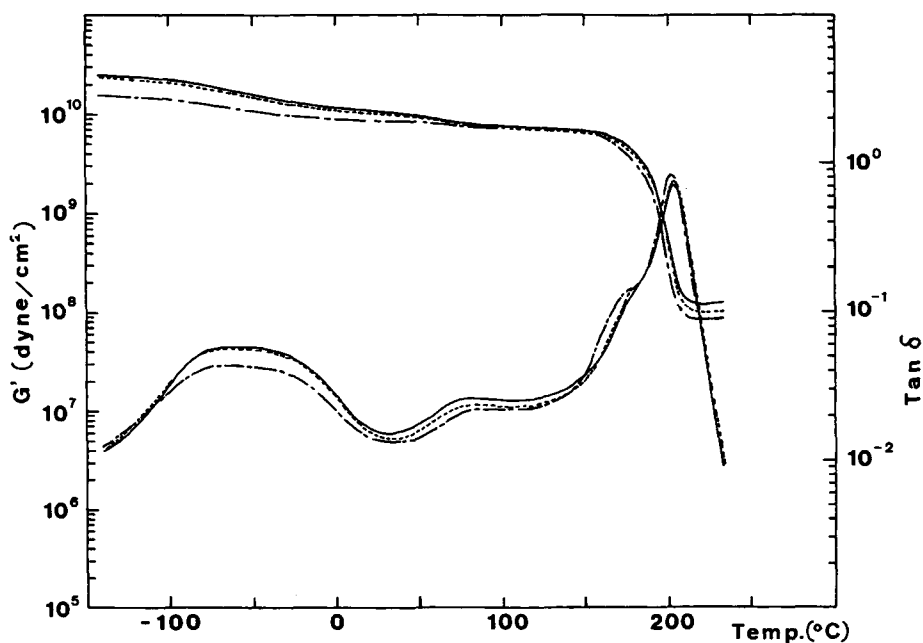


Figure 9 Dynamic viscoelastic analysis for PSC-4-modified cured resin. (—) control; (-----) 10 wt % addition; (- - -) 20 wt % addition.

cured resin and corresponds to the T_g value (128°C) of PSC 3 used and the morphology of the modified resin. In the modification with PSC 4 the peak position and shape of the α -relaxation in the $\tan \delta$ curve was hardly changed, compared to that for the parent epoxy resin (Fig. 9). A shoulder peak of a new relaxation emerged at ca. 175°C in the $\tan \delta$ curve and its magnitude increased with increasing PSC 4 content. This relaxation temperature corresponds to the T_g value (163°C) of the modifier. The storage modulus below 85°C decreased slightly in the modification with both PSC 3 and 4. These behaviors correspond to morphologies of the modified resins.

In conclusion, chloro-terminated polysulfones (PSC) were effective modifiers than epoxy-terminated polysulfones (PSE). These results would be attributed to the compatibilities of polysulfones used here with the cured epoxy resin system. The modification with PSC shows the importance of microphase-separated structures in the present system, though two-phase morphology is not necessary in the use of engineering thermoplastics as modifiers.¹¹ In this study the suitable composition for the modification of the epoxy resin was inclusion of 20 wt % of lower molecular weight PSC (M_w 5300).

Epoxy-terminated PES (M_n 7100) was a slight less effective modifier than the phenol hydroxy-terminated PES (M_n 8200) in the literature.⁵ This result might be explained by a difference in the compatibility of the polysulfones used with the epoxy matrix; the former (tetrafunctional) has higher compatibility than the latter (bifunctional) perhaps dependent on the function of reactive terminal groups of the polysulfones. There is room for further study in the modification with PSE. The use of PSE with higher molecular weight than 20,000 would improve the effectiveness as modifiers.

The authors thank Dr. Shinji Takeda (Hitachi Chemical Industry Co., Ltd.) for measurements of dynamic viscoelastic data.

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Received August 9, 1991

Accepted August 20, 1991