Chemical modification of matrix resin networks with engineering thermoplastics: 1. Synthesis, morphology, physical behaviour and toughening mechanisms of poly(arylene ether sulphone) modified epoxy networks

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Bisphenol A-based epoxy resins were modified with either phenolic hydroxyl or aromatic amine functionally-terminated poly(arylene ether sulphone) oligomers and thermally cured with 4,4′ diaminodiphenyl sulphone. The resulting networks displayed significantly improved fracture toughness, with little sacrifice in modulus. The bisphenol A-based polysulphones were molecularly miscible with the epoxy precursors over the entire range of compositions and molecular weights investigated, but developed a two phase structure upon network formation. The molecular weights and composition of polysulphone chemically incorporated into the network were varied and their effect on several important physical properties was investigated. The dynamic mechanical analysis and scanning electron microscopy (SEM) studies showed that it is possible to generate a two-phase morphology in the cured networks wherein polysulphone composite particles are dispersed in the epoxy matrix. Despite the two-phase structure, the modified crosslinked systems are nearly transparent, due to a similarity in component refractive index values. The fracture toughness of these modified networks under plane strain conditions improved significantly with minimal sacrifice of the flexural modulus.

(Keywords: bisphenol A-based networks; poly(arylene ether sulphone); matrix resin networks; chemical modifications)

INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers. These networks have many desirable properties which include high tensile strength and modulus, excellent chemical and corrosion resistance and good dimensional stability[1–3]. Consequently, these materials are widely used for many important applications such as coatings, structural adhesives, reinforced plastics and matrix resins for advanced composite materials[1–4]. Unfortunately, these highly crosslinked networks are inherently brittle and consequently have limited utility in applications requiring high impact fracture strength, or even thermal cycle resistance.

In recent years, the incorporation of elastomeric modifiers has served as a successful means of enhancing the fracture strength of brittle materials. The phase-separated rubber particles are presumed to act as stress concentrating sites, thus initiating energy absorbing 'toughening' processes such as crazing and shear band formation. This technology has been applied to epoxy resins through the utilization of low molecular weight liquid butadiene acrylonitrile copolymers having either carboxyl (CTBN) or amine (ATBN) reactive end groups[4–8]. Other elastomeric modifiers that have been studied include acrylate elastomers[8], poly(oxypropylene amines)[9] and polysiloxane copolymers[7,8]. The $K_{\mathrm{I,C}}$ fracture toughness values of the rubber modified epoxy networks are considerably higher in some cases than those for the unmodified materials. These $K_{\mathrm{I,C}}$ values were strongly dependent on the testing rate[6], temperature[10], crosslink density[11], volume fraction of rubber[6] and the type and structure of the curing agent[12]. The mechanism of energy dissipation for the crosslinked epoxy networks is different from that for linear rubber toughened thermoplastics and engineering polymers. For

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example, Kramer[13] has studied the fracture mechanisms of polystyrene of various molecular weights. At molecular weights above 30000, the approximate critical molecular weight for entanglements, $\bar{M}_c$, crazing was observed in the fractured samples. However, crazing was not important in fractured specimens at lower molecular weights where only local shear deformation was observed. Therefore, it is unlikely that highly crosslinked epoxy networks craze[6], and the only energy absorbing mechanism possible is localized plastic deformation.

Various theories have been proposed to explain the toughening effect of the rubbery particles on these highly crosslinked structures. Douglas[14] suggested that the rubber particle bridges the crack, before stretching and tearing of the rubber induces failure. Others have observed microcracking[15], crazing[16], and local shear[17] yielding, which is thought to be induced by stress concentrations of particles. Today, the most accepted theory involves the basic deformation processes and their interaction with the dispersed particles[6]. One process involves a dilation or void formation at the particle or its interface produced by triaxial stress ahead of the crack tip, along with the stresses induced by the presence of the particles. A second process involves initiation of shear deformations at the equator of the particles, where the stresses are the greatest. The latter process has been endorsed by many investigators to be primarily responsible for the toughening of many resin networks.

The improvement in fracture toughness by the addition of the rubber modifier is at the expense of bulk properties (i.e. modulus). This is not unexpected because the modulus of the modifier is much lower than the matrix. In principle, the use of hard or rigid particles may initiate some of the energy absorption mechanisms available to thermosets. Although there are several examples of toughening brittle materials with rigid particles, there are many problems associated with these systems. Bucknall[18] has investigated the possibility that glass particles could impact modify polystyrene, however, the fracture strength of these materials actually decreased. It is quite possible that poor interfacial adhesion between the particle and the matrix, as well as the brittle nature of the inorganic glass caused the decrease in impact strength. Similar effects have also been observed in both epoxy and polyester resins. The observation that rigid particles are not as effective as rubber fillers in increasing toughness may also be associated with the inability of a rigid particle to span and stabilize a craze[19].

Other investigations have shown that rigid particle-filled epoxy resins do show an improvement in fracture toughness. However, this improvement is largely dependent on the particle size and adhesion. For instance, Lange and Radford[20,21] used aluminium trihydrate to modify epoxy networks and found an enhancement in toughness which depended on volume fraction and particle size. They proposed the main energy absorption mechanism involved so-called 'crack pinning'[6,22]. As the crack approaches a layer of rigid particles, the crack front is 'pinned', perhaps due to the development of sufficient adhesion between the particle and the matrix. The crack is then 'bowed', thus creating new surface area before fracture. Typically, striations on the fracture surface have been reported where the pinning may have occurred.

Recently, another approach using rigid particles has been taken to modify epoxides. Physical blends of tough, ductile polyether sulphone and poly(ether imides) engineering thermoplastics have been reported by Bucknall[22] and Diament[23], respectively. However, Bucknall[22] reported that the addition of the polyethersulphone physically blended into the epoxy did not significantly improve the fracture toughness. Polyethersulphone is a polar material and actually has a higher solubility parameter than the epoxy network. Thus, although the solubility parameter difference promoted phase separation, it also limited the interfacial adhesion and consequently the fracture toughness. More importantly, the polysulphone modifier was simply physically blended into the epoxy resin and not chemically reacted, which also contributed to the poor interfacial adhesion and also loss of chemical resistance.

This paper will describe the use of phenolic hydroxyl and an aromatic amine-terminated polysulphone oligomer to chemically modify epoxy networks. The oligomers were reacted with a large molar excess of the epoxy resin and then cured into crosslinked networks with a stoichiometric quantity of 4,4'-diaminodiphenylsulphone (DDS). Several preliminary accounts of this work have already appeared[24–26] and this paper will describe details of the synthesis of oligomers, the curing chemistry of modified networks and some thermal, morphological and mechanical characterization of the resultant modified thermosets. Additional research is in progress and will be reported later.

EXPERIMENTAL

Purification of solvents and monomers

NMP (Fisher Scientific Company) was dried by stirring over phosphorus pentoxide (P_2O_5) or calcium hydride (CaH_2) for 24 h and then vacuum distilled at approximately 70°C to avoid degradation. High purity Bisphenol-A (Bis-A) was obtained from either Union Carbide Corporation or Dow Chemical Company and recrystallized from toluene. 4,4'-Dichlorodiphenyl sulphone (DCDPS) was kindly supplied by Amoco Corporation and was recrystallized from toluene. The diaminodiphenylsulphone (DDS) was obtained from Aldrich Chemical Company and used without further purification. The Epon resin 828 was kindly supplied by Shell Chemical Corporation (equivalent wt = 190 g mol^{-1}).

Polymer synthesis

Synthesis of hydroxyl-terminated polysulphone oligomers. A typical synthesis of a phenolic hydroxyl-terminated polysulphone oligomer was conducted in a four-neck, 500 ml round-bottom flask equipped with a mechanical stirrer, gas inlet, thermometer, Dean Stark trap, and condenser as described in an earlier publication[27]. For a synthesis designed to prepare a 14600 g mol^{-1} oligomer, the flask was charged with 22.83 g of Bis-A and 27.94 g of 4,4'-dichlorodiphenylsulphone. These monomers were carefully washed into the flask with NMP. The final volume of NMP was approximately 250 ml. To this solution, approximately 150 ml of toluene was added as an azeotroping agent. Finally, approximately 19 g of finely ground and dried potassium carbonate base was added. Note that the base was typically used in a 30 to 40% excess. This reaction mixture was then heated until the toluene began to reflux. An optimum reflux temperature range appears to be about 140–150°C. Water released during the phenoxide formation was azeotroped from the system. Refluxing must proceed until no more water is observed, which may take 3–5 h at these temperatures. The temperature was then increased to 180°C for 3–5 h. Completion or near completion may be qualitatively estimated by the point the viscosity increases dramatically. The polymer was then filtered, acidified and coagulated in a × 10 fold excess of a 50/50 methanol and water mixture. The polymer was then dried for 24 h in a vacuum oven at 80°C.

Modification and curing procedure using the phenolic hydroxyl-terminated polysulphone. A typical reaction between the phenol hydroxyl terminated-polysulphone and the Epon resin 828 was conducted in a 125 ml filtering flask equipped with a teflon-coated magnetic stirrer and a rubber stopper. Alternatively, a mechanical stirrer could be employed. To prepare a modified epoxy containing 15% by weight of polysulphone, 10.5 g (0.002 mol) of 5300 g mol^{-1} Bis-A polysulphone oligomer and 45 g (0.118 mol) of Epon 828 resin was charged along with 20–30 ml of methylene chloride into the flask. The large molar excess of the epoxy resin to that of the polysulphone oligomer is important. This stoichiometry will mainly result in the capping of the Bis-A–PSF oligomer, with minimal chain extension. Once the oligomers were dissolved in CH_2Cl_2 a trace amount ($\approx$0.2 wt%) of tetramethylammonium hydroxide in a 25% methanol solution was added as a catalyst for the epoxy–phenolic hydroxyl reaction. Other catalysts such as triphenyl phosphine can also be employed.

The mixture was then slowly heated under vacuum to 110–120°C for 4.5 h. At this time, the reaction mixture was clear and homogeneous. Once the reaction was considered to be complete, the temperature was increased to 160°C to completely decompose any residual transient quaternary catalyst. The reaction was then cooled to 150°C and the stoichiometric amount, 14.5 g (0.058 mol), of the curing agent 4,4′-diaminodiphenylsulphone was added. The reaction system was heated at this temperature under vacuum until it was homogeneous. It was then cooled to approximately 80°C, poured into a preheated silicone mould, cured at 140°C for 2 h and then post cured at 190°C for another 2 h. In some cases, the post cure was as high as 240°C oven after the curing cycles and cooled to room temperature. The networks prepared in the manner above were utilized for the thermal and mechanical characterizations studies discussed later.

Synthesis of high molecular weight poly(hydroxyether-sulphone) copolymers. The synthesis of control high molecular weight linear epoxy–polysulphone copolymer was conducted in a 250 ml four-necked round-bottom flask equipped with a mechanical stirrer, Dean Stark trap, condenser, thermometer and nitrogen inlet. In a typical reaction to prepare a high molecular weight epoxy–polysulphone copolymer, 3 g of 5300 g mol^{-1} polysulphone and 0.194 g of Bisphenol-A diglycidyl ether were charged to the flask. These materials were then washed down the flask with a 20 ml of dimethylsulphoxide. In order to dehydrate the system, 20 ml of toluene was used as a dehydrating agent. At this time, a trace amount ($\approx$0.2 wt%) of tetramethylammonium hydroxide was added to the system. The reaction mixture was heated to 115–120°C, where the DMSO–toluene mixture began to reflux. After 6 h, the reaction was extremely viscous and considered complete. The polymer was coagulated in a 50/50 mixture of methanol and water. The fibrous product was dried at 80°C under vacuum for 24 h.

Synthesis of amine-terminated polysulphone. α,ω-diamino poly(arylene ether sulphone) oligomers were initially prepared according to a published procedure[28]. A one litre, 5-neck flask fitted with an overhead stirrer, Dean Stark trap with a condenser, argon inlet, thermometer, and addition funnel was charged with 0.092 mol Bisphenol-A. It was dissolved in freshly distilled DMSO and toluene and 0.200 mol sodium hydroxide was added as a standardized 50 wt% solution. After complete addition of the base, 0.009 mol of the endblocker, more *p*-aminophenol was added. The system was allowed to dehydrate for 6 h, before 0.100 mol of 4,4′-dichlorodiphenylsulphone (DCDPS) was added and allowed to react for an additional 2.5 h at 170°C. This resulted in an amine-terminated poly(arylene ether sulphone) of approximately 5000 molecular weight ($\bar{M}_n$), as judged by titration. It is important to carefully dehydrate to optimize functionality.

Modification and curing procedures using the amine-terminated polysulphone oligomer. The amine-terminated polysulphone was added to the Epon resin 828 at 150°C and allowed to react for 10 min to allow good mixing. No catalyst was required in this case. The DDS was then added and the system was maintained at 150°C until homogeneous and clear. The reaction mixture was then cooled to approximately 80°C, poured into the silicone mould, cured for 2 h at 140°C, and post-cured 2 h at 190°C. Those networks which were modified with higher molecular weight oligomers required an additional post cure, 0.5 h at 205°C in order to develop their maximum transition temperature behaviour.

Characterization

Glass transitions, melting points and epoxy network curing investigations were determined using a Perkin–Elmer Model-2 DSC. The baseline was checked for flatness at each heating rate, and temperature calibration was accomplished using indium standards which have a known heat of fusion of 6.8 cal g^{-1}. Subambient transitions were achieved by immersing the cold finger in liquid nitrogen and purging the sample chamber with helium. Except where noted, the heating rate was 10°C min^{-1}. Intrinsic viscosities of the various polysulphone and related structures were determined using a Cannon–Ubbelohde dilution viscometer. Four concentrations of the polymer solutions in chloroform or NMP at 25°C were used for the measurement. Dynamic mechanical spectra of several of the modified networks were obtained using a Polymer Laboratories dynamic mechanical thermal analyser operating at 1 Hz. Materials were run in a single cantilever mode with a 1 mm free length, and a heating rate of 5°C min^{-1}.

In the h.p.l.c. analysis, a Waters M-45 solvent delivery system was used. A precolumn of 5 μ ODS packing 3 cm long with an inner diameter of 4.6 nm was used in conjunction with a DuPont Zorbax ODS column, 25 cm long with an inner diameter of 9.5 nm. A Waters Model R401 differential refractometer was used as the detector. A 20 μl sample loop was used to inject samples into the chromatography.

Titration of functional oligomers was carried out using a computer-interfaced Fisher Scientific Titrimeter II automatic titrator operating in the automatic endpoint seeking (AEP) mode. A standard calomel electrode was used with a double junction reference. The electrodes were stored in a pH 4.0 buffer. The electrometer was calibrated according to the manufacturer's instructions. A 10 ml burette was used for all titrations. The hydroxyl-terminated polyarylether sulphonic oligomers were titrated with 0.2 N aqueous tetraethylammonium hydroxide in 20 ml of either anhydrous *N*,*N*-dimethylformamide (DMF) or *N*,*N*-dimethylacetamide (DMAC) as reported earlier[29]. The amine-terminated oligomers were dissolved in chlorobenzene-glacial acetic acid (2:1 ratio) and titrated with a 0.2 N hydrobromic acid in glacial acetic acid.

Scanning electron microscopy (SEM) was used to study the nature of the domains by observing the K_{IC} fracture surfaces in the modified networks. An ISI Supper III was used with gold-palladium coated samples for most of the routine examinations of the fracture surfaces.

The plane strain fracture toughness, K_{IC}, is a very important parameter commonly used to describe a material's resistance to unstable crack propagation. In linear elastic fracture mechanics, the value K_I, the stress intensity factor, relates the elastic stress field intensification in the vicinity of the crack tip to the loading and specimen geometry of the sample. The value K_{IC}, fracture toughness indicates the critical stress intensity for a load which will cause catastrophic failure in mode I testing or tension. The value of K_{IC} varies with temperature, strain rate, and chemical environment. For our investigation, the three-point bend specimen geometry was used. The equation for K_{IC} for a three-point bend specimen is

$$K_{I,C} = 3PLa^{1/2}Y/Bw^2$$

where P = load; $L = 2w$; B = thickness; w = width; and a = crack length. Y is a geometric factor given by:

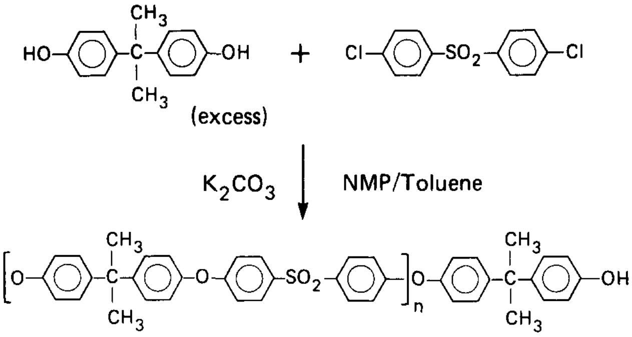
$$Y = 29.6 - 186(a/w) + 656(a/2)^2 - 1017(a/2)^3 + 639(a/w)^4$$

The criteria described in ASTM E394 were followed as closely as possible. The dimensions of the fracture toughness samples were approximately 3.2 × 6.4 × 38.1 mm. The precrack was introduced with a saw cut and then 'sharpened' with a new razor blade. The crosshead speed utilized was 0.5 mm min^{-1} for all samples tested.

The flexural modulus was determined using a three-point bend specimen geometry. The test specimens were 52.0 × 1.7 × 13.1 mm in size, and were tested with a crosshead speed of 1.0 mm min^{-1}.

RESULTS AND DISCUSSION

Hydroxyl-terminated bisphenol-A polysulphone (Bis-A PSF) oligomers were synthesized by a nucleophilic aromatic substitution reaction in *N*-methyl-2-pyrrolidone (NMP) in the presence of potassium carbonate (K_2CO_3) as shown in *Scheme 1*[27]. Toluene was used to azeotrope the water generated upon bisphenoxide formation. The Carothers equation was employed to calculate the excess of Bisphenol-A required to give the appropriate molecular weight and hydroxyl termination. Upon dehydration, the reaction was heated to 180°C to effect the displacement reaction. High molecular weight was obtained as judged by the viscosity increase (24 h). The oligomers were then isolated in excess methanol. *Table 1* contains the oligomers synthesized as well as the intrinsic viscosities, number average molecular weight as determined by end group analysis and glass transition temperatures.



Scheme 1

Table 1 Characteristics of hydroxyl-terminated polysulphone oligomers

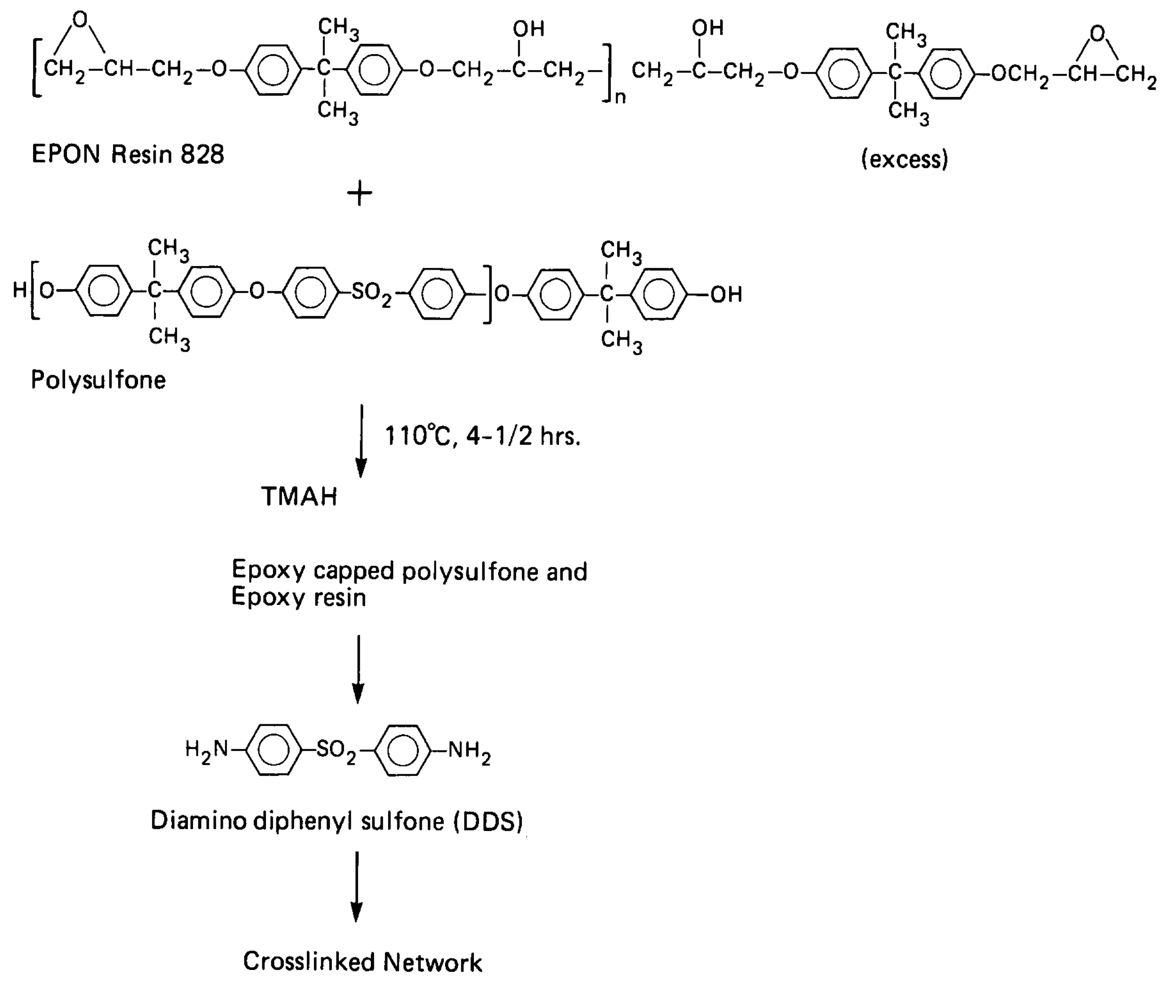
Number	M_n (g mol^{-1}) of PSF Theory	Via end group analysis[a]	T_g (°C)
1	3 000	3 100	165
2	5 000	5 300	180
3	7 000	6 200	180
4	10 000	8 200	183
5	15 000	14 600	189

[a] Potentiometric titration using TMAH

The preformed hydroxyl-terminated polysulphone oligomers were reacted with a large molar excess of Epon resin 828 in the presence of a catalytic amount of tetramethyl-ammonium hydroxide (TMAH). A large excess of epoxy resin was used to end cap the polysulphone oligomers which essentially prevents further polymerization. The reaction is illustrated in step 1 of *Scheme 2*. The PSF, Epon 828 and catalyst were homogenized in methylene chloride and a vacuum was then applied to remove the solvent. The mixture was heated and allowed to react for 4–5 h at 110°C to cap the PSF and then heated to 160°C for 3 h to decompose the quaternary-transient catalyst. The final step was to cure the modified resin with a stoichiometric amount of the 4,4'-diaminodiphenyl sulphone (*Scheme 2*, step 2).

In the first step of the reaction, the chemical incorporation of the polysulphone oligomer into the epoxy resin is considered to be crucial, because otherwise a simple physical blend would result. The chemistry of the phenoxide–epoxy reaction is fairly well understood. Commercially available polyhydroxyether is produced by Union Carbide which is known as phenoxy resin. Several techniques were used to characterize and monitor this reaction.

Reverse phase h.p.l.c. was used, in an attempt to more accurately assess the modification of the epoxy resin with polysulphone. Four samples were prepared for this investigation; the Epon resin 828, the polysulphone oligomers, blends of the epoxy and polysulphone oligomers and the chemical modification of the epoxy resin with the polysulphone oligomer. The retention times for these samples depend on their interaction with the column. *Figure 1* shows the h.p.l.c. chromatograms for



Scheme 2

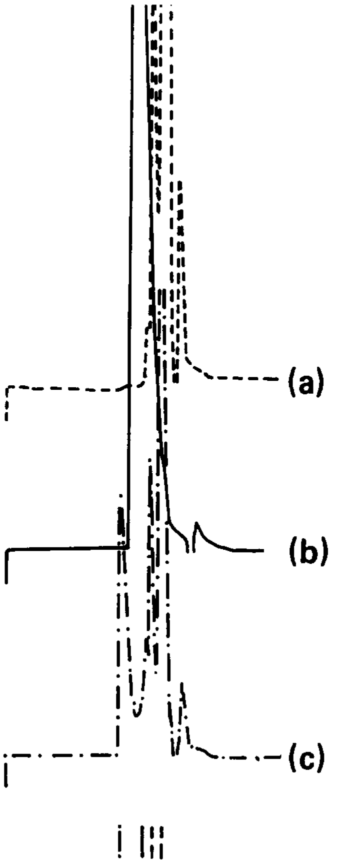
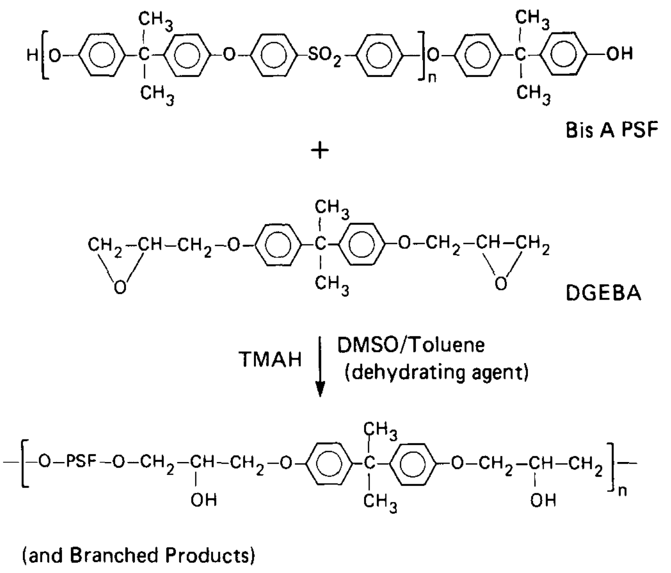


Figure 1 H.p.l.c. chromatograms for curve (a) Epon Resin 828, curve (b) polysulphone oligomer (5300$\langle M_n \rangle$) and curve (c) Epon Resin 828 modified with 5300$\langle M_n \rangle$ polysulphone (10 wt% polysulphone)

Epon resin 828, polysulphone oligomer (5300 g mol^{-1}) and modified resin. The Epon resin 828 (curve a) gives two peaks indicating that the degree of polymerization, *n*, can be 1 or 2, as shown below. Blends of the polysulphone and epoxy oligomers gave identical retention times as those of the starting oligomers (curves a and b). However, in the case c, the polysulphone (5300 g mol^{-1}) modified epoxy resin, a new peak developed strongly supporting the position that a reaction had indeed occurred. Furthermore, the peak corresponding to the polysulphone oligomer was no longer present, leading us to believe the capping reaction was both successful and quantitative.

The previous experiments demonstrated that the chemical modification of the functionally-terminated polysulphone oligomers with a large molar excess of Epon resin 828 was successful. However, to better understand the chemistry of these systems, linear poly(hydroxyether-sulphone) copolymers were synthesized by reacting the phenolic hydroxyl polysulphone oligomers with a stoichiometric amount of DGEBA, as shown in *Scheme 3*. Dimethylsulphoxide was chosen as the solvent because it is sufficiently polar to solvate the starting materials, polar intermediates, and the high molecular weight copolymer. The strong base, TMAH, was used in a catalytic amount to convert the phenolic hydroxyl end groups on the polysulphone oligomer into its more reactive bisphenoxide. *Table 2* contains the polymers synthesized along with their glass transition temperatures and intrinsic viscosities. In each case, high molecular weight was obtained as determined by intrinsic



Scheme 3

Table 2 Characteristics of segmented poly(hydroxyether)–polysulphone copolymers

Sample	M_n polysulphone oligomer	$[\eta]CHCl_3$ (25°C)	T_g (°C)
1	5300	0.6	187
2	9700	0.9	187

viscosity measurements and film characteristics. G.p.c. chromatograms of the starting oligomers (*Table 1*) and high molecular weight epoxy–polysulphone copolymers (*Table 2*) are shown in *Figures 2* and *3*, and in each case, the copolymers were shifted to lower elution volumes indicating a higher molecular weight. In addition, copolymer 2 (*Table 2*) showed a broad bimodal molecular weight distribution indicative of branching, presumably at the secondary hydroxyl group.

The polysulphone modified epoxy resins were cured with a stoichiometric amount of 4,4′-diaminodiphenylsulphone (DDS), as illustrated in step 2 to *Scheme 2*. The networks synthesized as well as the composition and block molecular weight of the polysulphone modifier are given in *Table 3*. In each case, either 10 or 15% by weight of polysulphone oligomer or polymer was reacted or blended into the epoxy network. The molecular weight and weight percent polysulphone added influenced the curing procedure utilized. The modified networks were cured at 140°C for 2 h and then 195°C for 2 h. However, a second post-cure was required for networks containing the higher molecular weight oligomers (numbers 8 and 9 in *Table 3*). Extremely high melt viscosities were associated with these modified epoxy resins. In fact, those resins which contained higher molecular weight polysulphone oligomers were solid at room temperature and did not flow until 40°C. *Table 3* also contains the glass transition temperatures of these networks. D.s.c. scans do not show any further exotherms which indicate that these systems are fully cured.

The basic approach employed here in modifying the epoxy resins with polysulphone oligomers has some similarity to the ATBN, CTBN and siloxane rubber modifiers. In these systems, the solubility parameter is controlled in such a way that these oligomers are miscible with the epoxy resin in the initial stages of the cure but will phase separate during the later stages. In the present system, the solubility parameters are such that the polysulphone is miscible with the epoxy resin in the first

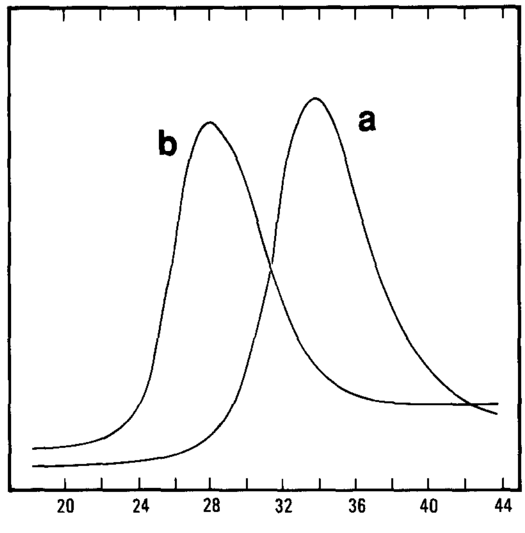


Figure 2 G.p.c. chromatograms of (a) $5200\langle M_n \rangle$ polysulphone oligomer and (b) high molecular weight hydroxyether–sulphone copolymer

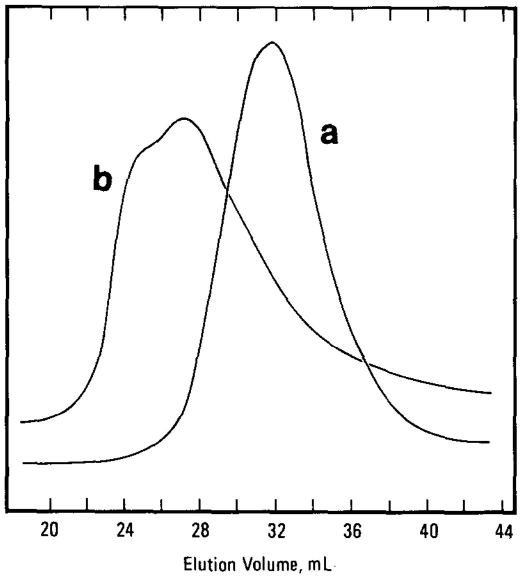


Figure 3 G.p.c. chromatograms of (a) $9700\langle M_n \rangle$ polysulphone oligomer and (b) high molecular weight hydroxyether–sulphone copolymer

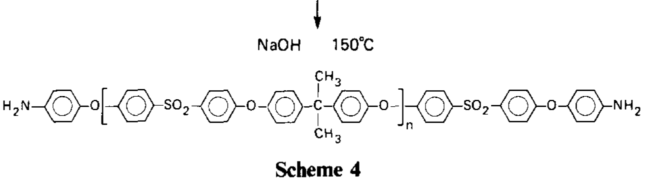
Table 3 Characteristics of bis-A polysulphone modified epoxy networks

	Modifier			Network
Number	M_n ($g\,mol^{-1}$)	T_g (°C)	wt%	T_g (°C)
1	3 100	–	15	187
2	5 300	180	10	–
3	5 300	180	15	–
4	6 200	180	10	187
5	6 200	180	15	192
6	8 200	183	10	198
7	8 200	183	15	200
8	14 600	189	10	196
9	14 600	189	15	198

stage of the reaction and produces a clear homogeneous solution. This good mixing promotes the chemical reaction and network formation. During the curing process, as the molecular weight increases, the thermoplastic component separates within the reaction medium to form a second dispersed phase. The solubility parameter of the epoxy resin has been previously estimated to be 9.4 which is lower than that of the bisphenol-A-based polysulphone, 10.2. No doubt, this difference assists in the phase separation of the components, as observed in SEM studies to be discussed later in the paper.

Our second example involves the use of amine terminated PSF oligomers and in contrast to the two step process of the first example the amine-terminated polysulphone oligomers may be used together with the curing agent, diaminodiphenyl sulphone, in a one-step modification process. Amine-terminated bisphenol-A-based polysulphone (Bis-A PSF) oligomers of predictable molecular weight were successfully synthesized via nucleophilic aromatic substitution using a modified Carothers equation as shown in *Scheme 4*. *Table 4* shows the molecular weight and glass transition temperatures of the various amine-terminated polysulphones synthesized.

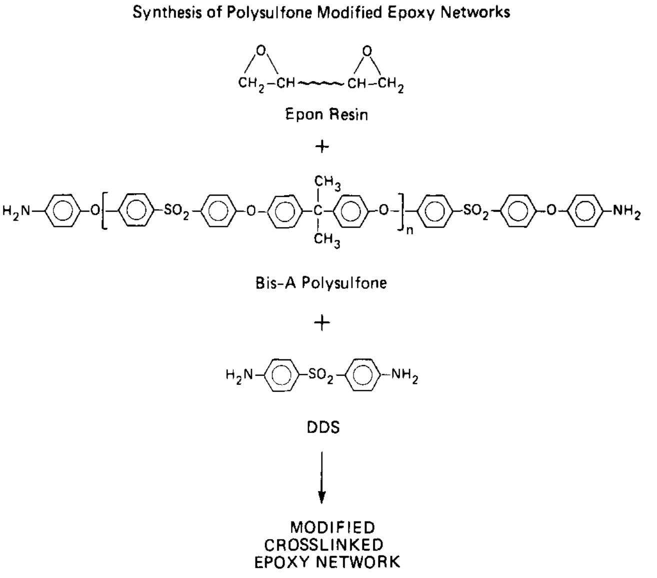
The amine-terminated polysulphones were used together with diaminodiphenyl sulphone to cure Epon resin 828 as shown in *Scheme 5*. *Table 5* contains the thermal properties of the final modified networks and for comparison, networks of Epon resin 828 cured with DDS. In each case, the amount of polysulphone used to modify the network was initially held at 15 wt%. In both the control and the modified networks, the T_g values are in the 190–200°C range. The d.s.c. scans show no exotherms after the T_g, which clearly indicates that the curing was complete.



Scheme 4

Table 4 Characteristics of amine-terminated polysulphone oligomers

Number	M_n (g mol^{-1})	$[\eta]^{25°C}_{CHCl_3}$	T_g (°C)
1	4 100	0.16	148
2	7 100	0.18	167
3	13 100	0.22	178



Scheme 5

Table 5 Thermal properties of networks modified with amine terminated PSF oligomers

Number	PSF M_n (g mol^{-1})	PSF (wt%)	Network T_g (°C)
1	Epon resin 838/ DDS control	0	195
2	4 100	15	193
3	7 100	15	187
4	13 100	15	190

The main objective of this investigation was to improve the toughness of the epoxy networks by the addition of the ductile polysulphone at a minimum sacrifice to the modulus. In contrast, the conventional rubber modifiers typically show improved fracture properties at the expense of the modulus. The $K_{I,C}$ values for the phenolic hydroxyl-terminated polysulphone modified epoxy networks are given in *Table 6*. There are several important observations to be made. First, as the amount of polysulphone is increased in the matrix the fracture toughness increases as well. In addition, as the block length of the polysulphone oligomer increases, the fracture toughness first increases and then levels off. Unlike the rubber modifiers, polysulphone is a high T_g ductile engineering thermoplastic with a high modulus at ambient temperature. Therefore, it is not surprising that the bulk properties in these modified networks are better retained. *Table 6* also contains the flexural modulus of the control and the modified networks. In each case, the modulus of the polysulphone modified networks only decreased about 10–15%, which is considerably better than the rubber modifiers.

In a similar fashion, the amine-terminated polysulphone modified network also showed an improvement in fracture toughness. *Table 7* gives the $K_{I,C}$ values for the neat and the modified networks synthesized by a one-step process. The polysulphone content was held constant at 15 wt% in each case. The fracture toughness appears to be sensitive to the molecular weight and composition of the oligomer. This is consistent with fracture toughness values for the phenolic hydroxyl-terminated modified networks. In addition, only a small sacrifice in flexural modulus was observed for each of these modified networks as shown in *Table 7*.

To further illustrate this point, *Figures 4–6* contain dynamic mechanical spectra of a 8200 g mol^{-1} phenolic

Table 6 Mechanical properties of hydroxyl functional bis-A polysulphone modified epoxy resins

Number	PSF M_n	PSF (wt%)	Flexural modulus ($N m^{-2}$)	Fracture toughness, $K_{I,C}$ ($N m^{-3/2}$)
1	Control		2.5×10^9	0.6×10^6
2	3100	15	2.1×10^9	0.6×10^6
3	5300	10	2.0×10^9	0.9×10^6
4	5300	15	2.0×10^9	0.9×10^6
5	6200	10	1.9×10^9	0.9×10^6
6	6200	15	2.3×10^9	1.1×10^6
7	8200	10	–	1.0×10^6
8	8200	15	2.2×10^9	1.3×10^6
9	14600	10	2.2×10^9	1.0×10^6
10	14600	15	2.3×10^9	1.2×10^6
11	polysulphone control			2.4×10^6

Table 7 Mechanical properties of amine terminated polysulphone modified epoxy resins

Number	PSF M_n ($g mol^{-1}$)	PSF (wt%)	Modulus ($N m^{-2}$)	Fracture toughness, $K_{I,C}$ ($N m^{-3/2}$)
1	Epon resin 828/DDS control	–	2.5×10^6	0.6×10^6
2	4100	15	1.8×10^9	0.8×10^6
3	7100	15	–	0.8×10^6
4	13100	15	1.9×10^9	0.8×10^6

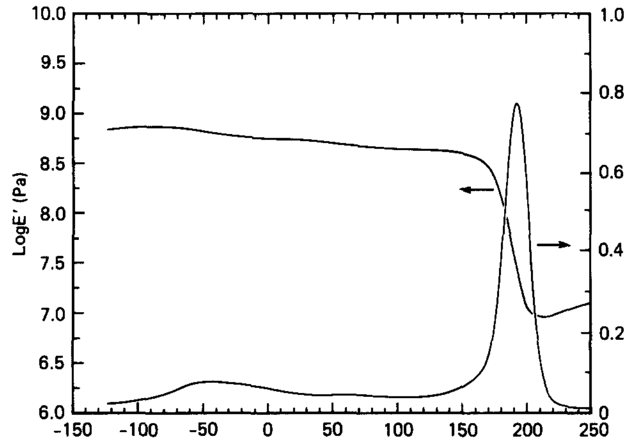


Figure 4 Dynamic mechanical thermal analysis of 8200$\langle M_n \rangle$ phenolic hydroxy-terminated polysulphone modified epoxy network (15 wt% PSF) measured at 1 Hz

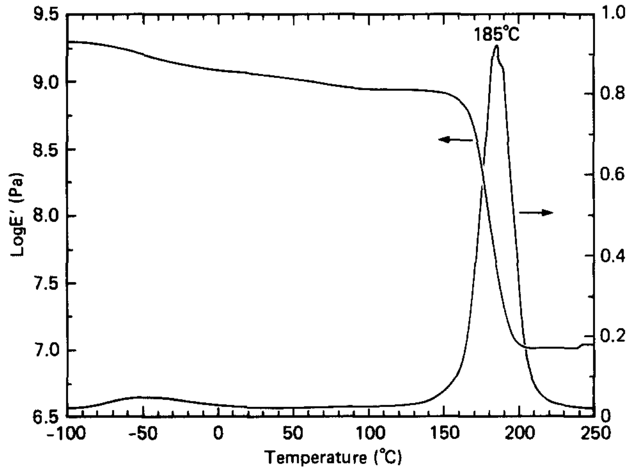


Figure 5 Dynamic mechanical thermal analysis of 13100$\langle M_n \rangle$ amine-terminated polysulphone modified epoxy network (15 wt% PSF) measured at 1 Hz

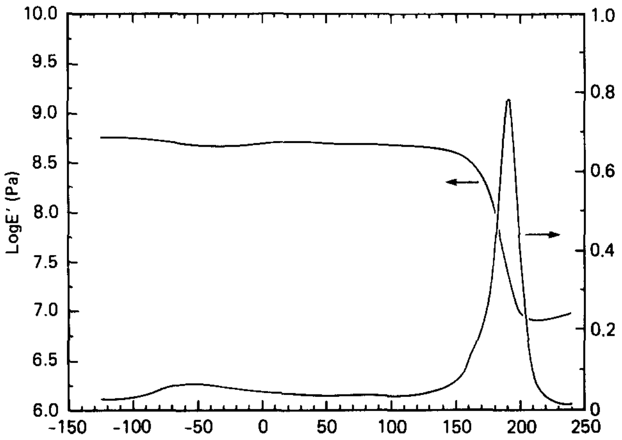


Figure 6 Dynamic mechanical thermal analysis of the control (Epon Resin 828 cured with DDS) measured at 1 Hz

hydroxyl-terminated polysulphone modified network, a 13300 g mol^{-1} amino-terminated polysulphone oligomer and a control (Epon 828 cured with DDS), respectively. For each sample, a high modulus may be observed up to the T_g of the epoxy network. This is not typical of the rubber modified systems. Each of these materials also shows a large damping transition in the 190–195°C range which is attributed to the T_g of the epoxy network. The glass transition temperature of the polysulphone is in the same temperature range and generally cannot be detected. However, the glass transition temperature of the polysulphone oligomers are molecular weight dependent up to a number average molecular weight of 12000–14000 g mol^{-1} range. The large tan δ in the 8200 g mol^{-1} polysulphone modified network (*Figure 4*) shows a small shoulder on the major damping peak of the epoxy T_g. Assuming this is the glass transition temperature of polysulphone, this data suggests a two-phase morphology. The next section will discuss the morphology in more detail.

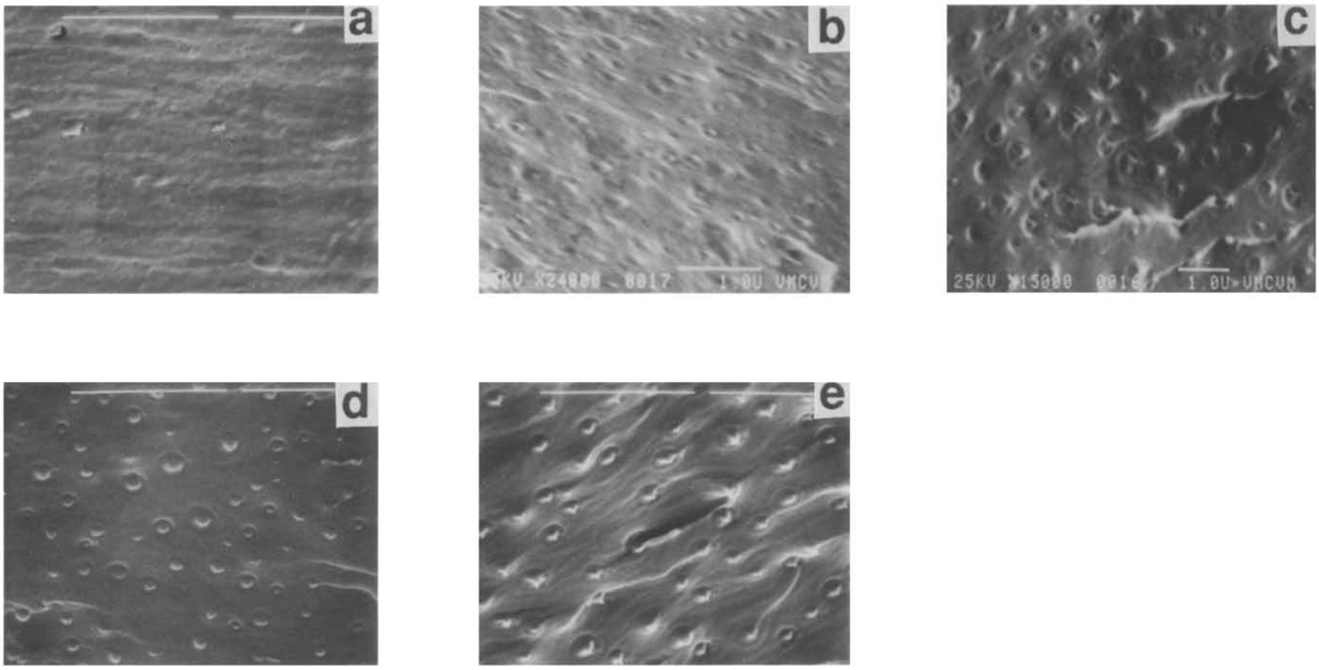


Figure 7 SEM micrograph of (a) 3100$\langle M_n \rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF); (b) SEM micrograph of 5300$\langle M_n \rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF); (c) SEM micrograph of 6200$\langle M_n \rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF); (d) SEM micrograph of 8200$\langle M_n \rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF); and (e) SEM micrograph of 14 600$\langle M_n \rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF)

In a close examination of the fracture surfaces with scanning electron microscopy (SEM), the two-phase morphology alluded to by the dynamic mechanical results is confirmed. *Figure 7* illustrates SEM micrographs of the phenolic hydroxyl-terminated polysulphone by weight. For the networks containing the 3100 g mol^{-1} polysulphone oligomer, single-phase morphologies were observed by this technique. However, for the 5300 g mol^{-1} polysulphone oligomer, a two-phase morphology is observed by microscopy, and this two-phase morphology becomes more pronounced and defined with increasing polysulphone molecular weight. In addition, as the molecular weight of the functional modifier increased, the average particle size increased from 0.3 to 0.8 μm for the 5300 to the 14 600 g mol^{-1} modified networks and as the composition of polysulphone incorporated into the network increased from 10–15% by weight, the frequency of particles increased. In each case, there exists both an even distribution and size of the particles within the matrix. *Figure 8* contains low magnification SEM micrographs of phenolic hydroxyl (8200 g mol^{-1}) and an amine (13 100 g mol^{-1}) terminated polysulphone oligomers which clearly illustrate this point. In addition, these micrographs show definite patterns and a rough surface which is generated with increasing thermoplastic molecular weight and content. Finally, in those samples containing higher molecular weight modifiers, small rings around each particle were observed.

Figure 9 contains the SEM micrographs of the amine-terminated polysulphone modified networks. This one-step modification process also produced a two-phase morphology when polysulphone oligomers of sufficient molecular weight were used. The higher molecular weight modifiers produced a two-phase morphology consisting of polysulphone composite particles embedded within the epoxy matrix. As in the previous case, the particles were

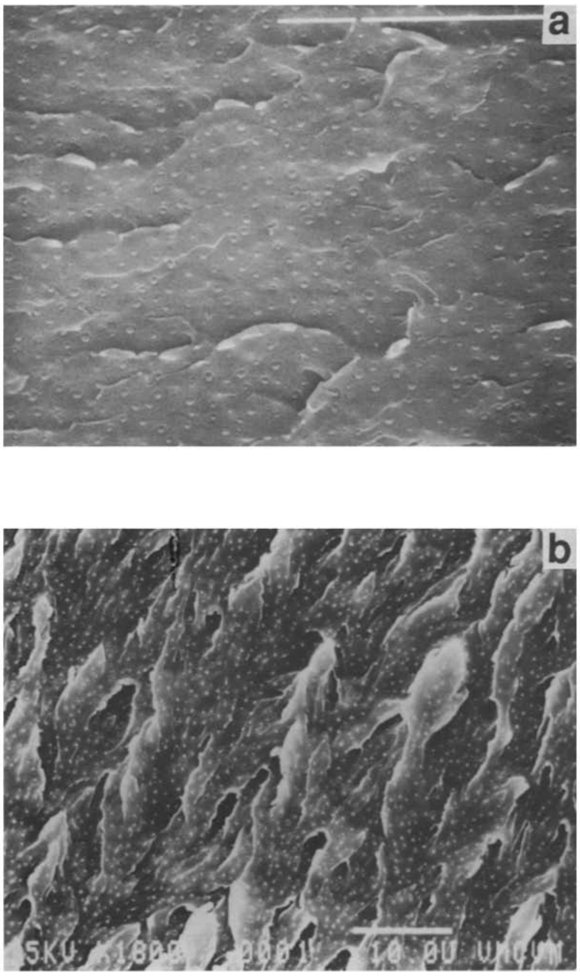


Figure 8 SEM micrograph of (a) 8200$\langle M_n \rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF), and (b) SEM micrograph of 14 600$\langle M_n \rangle$ amine-terminated polysulphone modified network (15 wt% PSF)

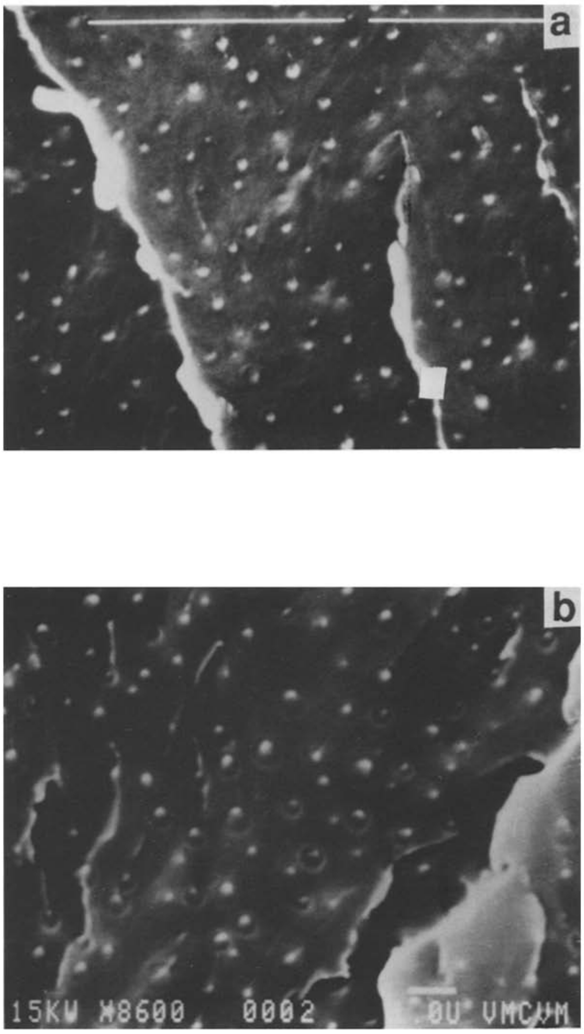


Figure 9 SEM micrograph of (a) $7100\langle M_n\rangle$ amine-terminated polysulphone modified network (15 wt% PSF), and (b) SEM micrograph of $13\,100\langle M_n\rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF)

of even distribution and size and showed the small rings around the particles. However, this dispersed phase is somewhat smaller than that generated for two-step modification process. It is conceivable that in the two-step process chain extension may occur, resulting in a higher molecular weight modifier and kinetic effects which control the domain size.

The fracture surface of a typical rubber toughened epoxy network generally consists of holes which contain rubber. The toughening of these materials is thought to result from a cavitation/ dilatation mechanism, and this has been reviewed by Kinloch[30]. The SEM micrographs of the polysulphone modified networks reveal particles on each side of the fracture surface with no corresponding holes. The thermal coefficients of expansion are very similar for each of the two components, precluding dilatation of the particle. It is proposed that the mechanisms for toughening of these systems are different than those for the rubber modified systems. The first observation made is that small rings surround each of the composite particles. The first observation made is that as the molecular weight of the polysulphone oligomer increases, the size of the particle increases. In addition, the fracture toughness also increases and levels off with increasing molecular weight of the polysulphone modifier. Furthermore, when these modified networks are viewed at an angle, the composite particles appear to be plastically deformed and even drawn. This effect is particularly pronounced when the highest molecular weight polysulphone oligomer was used, 14 600 g mol^{-1}. *Figure 10* contains a high magnification SEM micrograph of this sample. In fact, the polysulphone oligomer used here was of sufficient molecular weight to give a glass transition temperature similar to the commercially available, high molecular weight polysulphone, Udel. Films of the oligomer alone showed tough, ductile mechanical properties. To help confirm the observation, the fractured sample was heated above the T_g of the polysulphone (195°C) for 20 min. If the polysulphone had undergone plastic flow, it should then be expected to relax with this treatment. *Figure 11* contains a SEM micrograph at 60° of the 14 600 M_n polysulphone modified network after heating. As expected, the polysulphone composite particles relaxed and even flowed due to the thermal treatment.

It is proposed that the toughening of these network structures by addition of the polysulphone results in part from ductile nature of the polysulphone rich composite particles perhaps resulting in crack pinning, as previously discussed. It follows that as the molecular weight of the

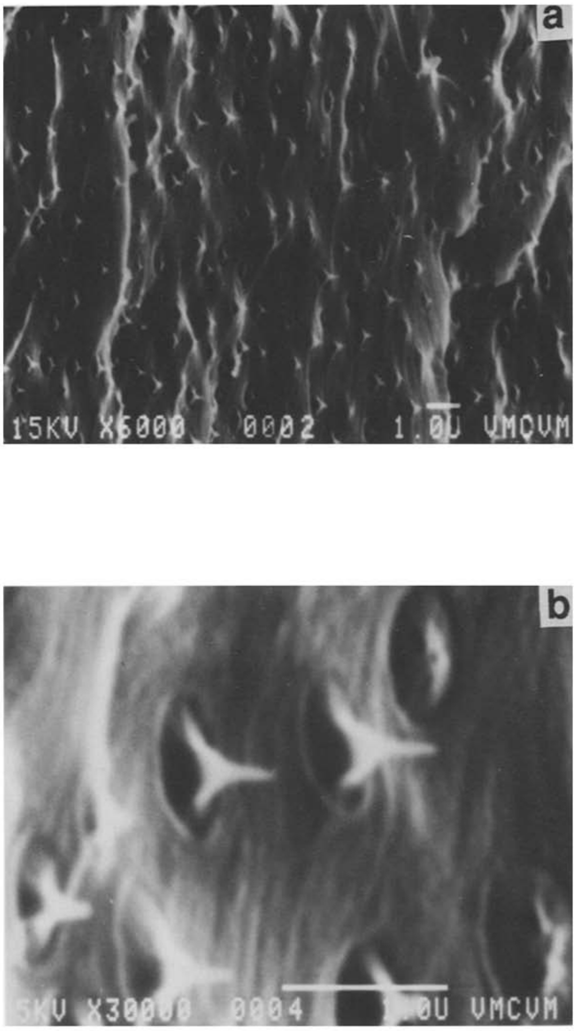


Figure 10 SEM micrograph of $14\,600\langle M_n\rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF). (b) Higher magnification of (a)

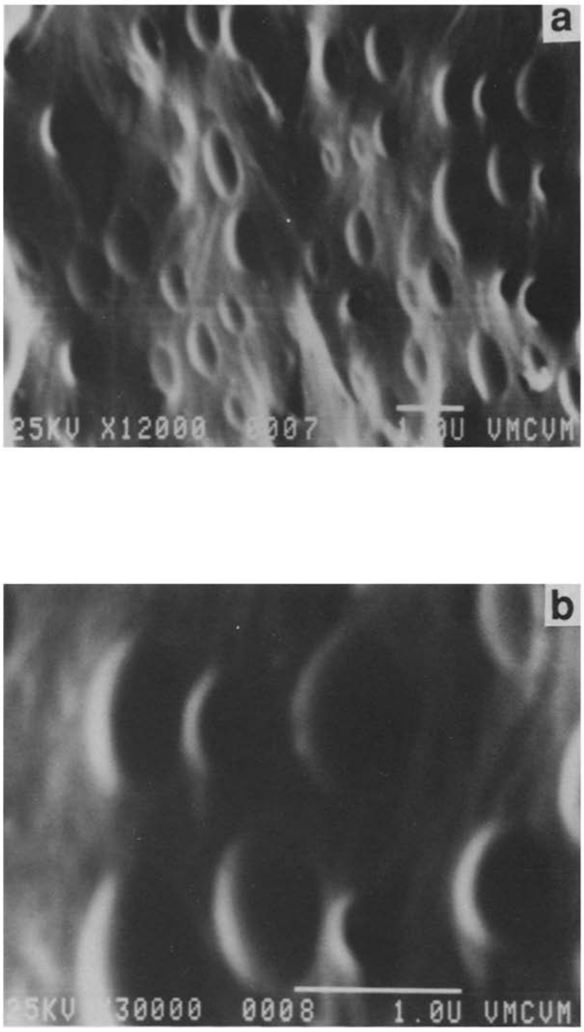


Figure 11 SEM micrograph of 14600$\langle M_n \rangle$ phenolic hydroxyl-terminated polysulphone modified network (15 wt% PSF) after heat treatment (195°C for 20 min). (b) Higher magnification of (a)

polysulphone increases and approaches the critical molecular weight for ductile properties, the fracture toughness of the modified networks increases as well.

Furthermore, a closer examination of the SEM micrographs of those networks modified with the higher molecular weight polysulphone oligomers have small rings around each of the particles. It has been noted by several authors that particles having a different modulus than the matrix serve as stress concentrators. Theories such as the cavitation/dilatation concept reviewed by Kinloch[33] propose that this stress concentration may plastically deform the local area surrounding the particle. Kramer and co-workers[31] found that the size of the discrete phase influences the efficiency of the initiation of the energy absorption mechanisms. The only energy absorption mechanism available to highly crosslinked epoxy networks is local plastic deformation, and small particles are more efficient at initiating these mechanisms. The optimum particle size found for these networks is in the 1.0–1.5 μm range. We believe that the thermoplastic composite particles promote local plastic deformation in the matrix, but the mechanism may be somewhat more complicated. However, polysulphone modifiers of low molecular weight ($<3000\ \mathrm{g\ mol^{-1}}$) are miscible with the epoxy network. The relatively broad molecular weight distribution ($M_w/M_n = 2$) associated with the polysulphone allows some amount of the modifier to remain somewhat miscible with the matrix, which may also influence the toughening behaviour.

Not only does the molecular weight of the oligomers used play a significant role in determining the fracture properties, but, as one may expect, the amount of these modifiers in the matrix also improves the fracture properties. This increase is only noticed for those samples with higher molecular weight blocks. In addition, as the frequency of the particles increases, it has been reported that the stress fields created by each particle interact, resulting in improved fracture toughness. Another important factor believed to be responsible for the improved impact strength is the good interfacial adhesion between the particle and the matrix due to chemical linkage. Previous attempts to modify brittle materials with hard particles such as glass may have failed because of poor interfacial adhesion.

In the previous examples interfacial adhesion was forced because of the chemical linkage and partial miscibility between the two components. If a blend of the non-reactive commercial Udel gives similar properties, it would be most advantageous in terms of both economics and time. Udel is largely methoxy end capped, thus precluding any reaction with the epoxy resin. Buchnall[22] modified epoxy networks with polyether sulphone (Victrex) but found little or no improvement in fracture properties. Polyether sulphone has a higher solubility parameter (11.2) than Bis-A PSF (10.2) which may have prevented good interfacial adhesion.

Blends of Udel and Epon Resin 828 were prepared as described in the experimental section. The modified resin 10 or 15% by weight polysulphone was then cured with a stoichiometric amount of diaminodiphenyl sulphone

Table 8 Thermal properties of Udel polysulphone physically modified networks

Number	Udel[a] (wt%)	Network T_g (°C)
1	Epon resin 828/DDS (control)	195
2	10	197
3	15	195

[a] Amoco Chemical Corporation

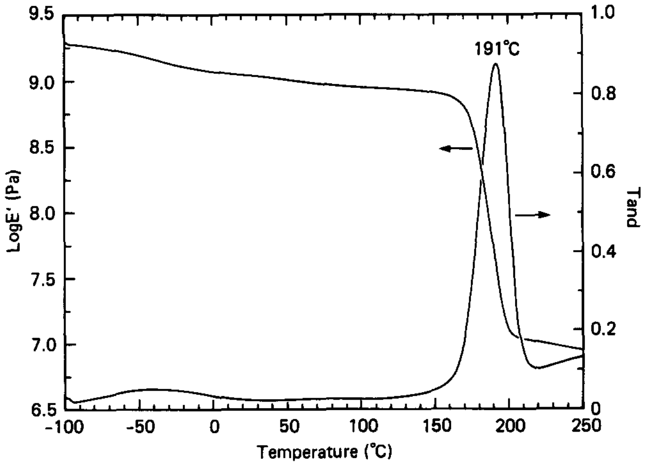


Figure 12 Dynamic mechanical analysis of Udel modified network at 1 Hz (15 wt% PSF)

Table 9 Mechanical properties of Udel modified epoxy networks

Number	wt% Udel	Flexural modulus (N m^{-2})	Fracture toughness, $K_{I,C}$ (N m$^{-3/2}$)
1	Epon resin/DDS (control)	2.5×10^9	0.6×10^6
2	10	2.1×10^9	0.8×10^6
3	15	1.9×10^9	1.1×10^6

into a highly crosslinked network. An additional post-cure (see experimental) was required because of the network glass transition temperature and the high viscosity associated with the modified resin. The thermal properties of the blends are shown in *Table 8*. In each case the data demonstrate that high glass transition temperatures were obtained which are comparable to the control.

Table 9 provides the flexural modulus and fracture toughness values for the modified resins. The fracture toughness of the physical blend also increased with the modifier in a similar fashion to the chemically reacted systems. However, later experiments demonstrated that the reactive system had poor chemical resistance and was also more dependent on mixing conditions. The addition of the modifier only caused a minimal sacrifice in the flexural modulus as illustrated in *Table 9*. This is further illustrated in the dynamic mechanical spectra (*Figure 12*). The T_g of the sulphone is again the same region as the epoxy network transition.

Figure 13 contains an SEM micrograph of a $K_{I,C}$ fracture surface of an Udel modified network. Discrete composite particles range from 0.8–1.0 μm in size. However, good interfacial adhesion was not observed in this case and holes were even present. This was confusing in light of the improvement in fracture toughness. A closer examination of the fracture topography revealed large 'globular' regions indicative of mixing variations. *Figure 14* contains such a region. These regions were easily removed upon treatment with chloroform, which suggests that they are regions of unmixed or at least heterogeneous polysulphone rich phases. *Figure 15* shows a treated fracture surface which consisted only of holes. It is interesting that these particular samples become opaque upon treatment with solvent but the chemically reacted materials do not. The toughening in these systems probably does not result from the composite particles per se. Regions of plastic deformation of the matrix in the vicinity of the particle were not observed, nor was the adhesion sufficient to allow ductile tearing or drawing of the polysulphone. The regions of unmixed polysulphone are believed to contribute to the improvement in fracture toughness. However, chemical resistance is poor.

CONCLUSIONS

Epoxy resins were modified with either phenolic hydroxyl or aromatic amine terminated aryl ether sulphone oligomers and thermally cured with 4,4′-diaminodiphenyl sulphone. The aryl ether sulphone oligomers were miscible with the epoxy precursor and upon network formation a two-phase structure developed in which the polysulphone formed discrete composite particles evenly dispersed in the epoxy matrix. The resulting networks showed significantly enhanced fracture toughness which probably results from the polysulphone particles which

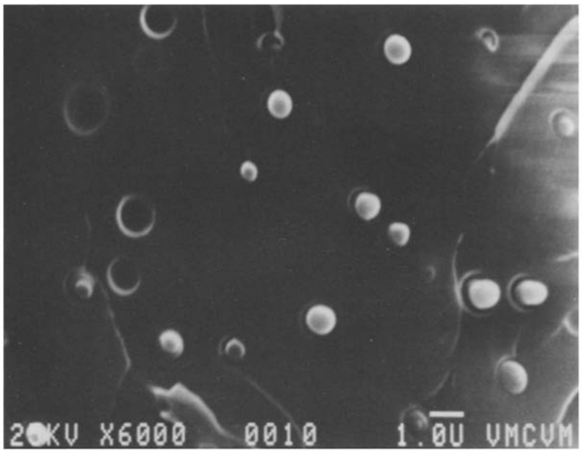


Figure 13 SEM micrograph of a Udel modified epoxy network (15 wt% PSF)

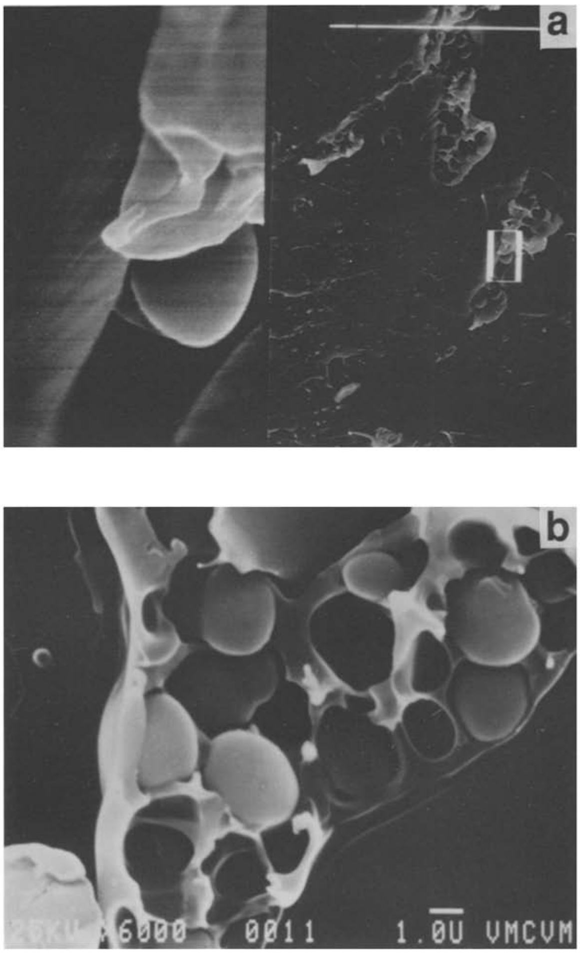


Figure 14 SEM micrograph of a Udel modified epoxy network (15 wt% PSF)

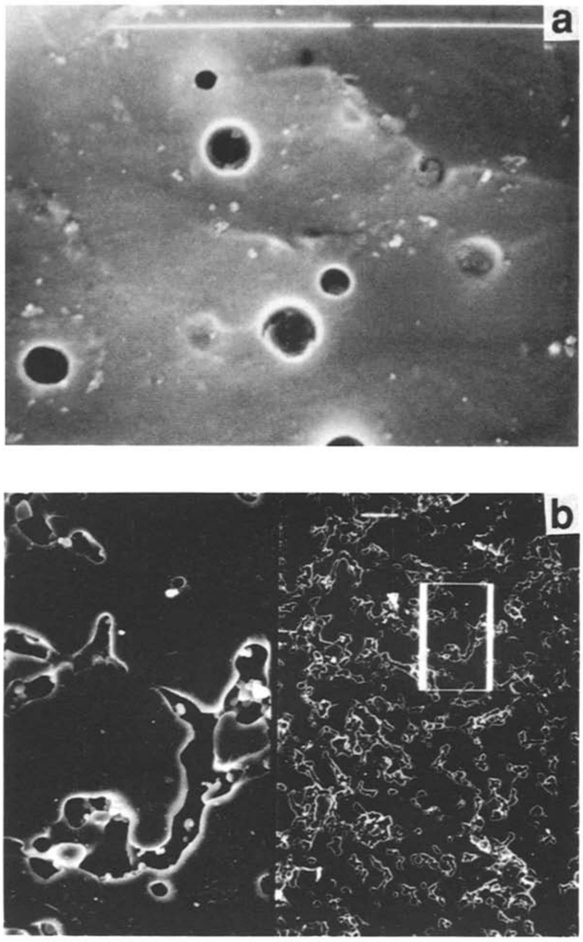


Figure 15 SEM micrograph of Udel modified epoxy network (15 wt% PSF) after solvent treatment

plastically deformed upon fracture as well as induced a local plastic deformation in the epoxy matrix.

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