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Amorphous phenolphthalein-based poly(arylene ether) modified cyanate ester networks: 1. Effect of molecular weight and backbone chemistry on morphology and toughenability

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Low toughness is a major drawback with most cross-linked thermosetting materials, including the cyanate ester networks. Reactive functional thermoplastic toughness modifiers not only enhance toughness but also permit highly desirable stability to solvent stress cracking without seriously affecting the moderately high modulus. Careful control of the heterophase morphological structure is necessary to achieve significant toughening. In the present work, hydroxyl functional phenolphthalein-based amorphous poly(arylene ether ketone)s, poly(arylene ether sulfone)s and poly(arylene ether phosphine oxide)s were investigated as potential toughness modifiers for the bisphenol-A based cyanate ester networks. In particular, the use of poly(arylene ether sulfone)s resulted in remarkable improvements in toughness. Multiphase networks were generated without compromising either T_g or the moderately high modulus of the unmodified cyanate ester networks. It was demonstrated that the toughenability of these systems is governed by microphase-separated morphologies and the sizes of the phase-separated domains. The formation of these heterophase morphological structures is strongly influenced by the backbone chemistry and the molecular weight of the thermoplastic modifier, probably via control of the polymer–polymer interaction parameter. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: cyanate ester networks; reactive thermoplastic poly(arylene ether sulfone); toughners)

INTRODUCTION

Epoxies and bismaleimides are examples of important thermosetting materials for high-performance adhesives and composite matrix applications[1]. Tightly cross-linked networks can be achieved which combine good thermal and mechanical properties with outstanding adhesive properties. However, their widespread use is unfortunately limited in many applications by their inherent brittle behaviour.

Initial attempts to impart ductility or increased impact strength to cured epoxy resin systems used various levels of 'reactive flexibilizers' or 'non-reactive plasticizers' based on long-chain epoxidized glycols and dimer acids[2]. However, the use of most of these modifiers resulted in drastic reductions in heat deflection temperature and strength.

Traditional toughness modifiers such as carboxyl-terminated butadiene–acrylonitrile copolymer rubbers (CTBN) have been widely reported[3–8] to improve toughness and in fact some important systems exist. However, such improvements were achieved at the expense of high-temperature performance. This has been attributed to the low glass transition temperature of the unsaturated rubbery phase, which lowers the end-use temperature and the modulus of the resulting networks. A two-phase morphology consisting of relatively small (0.1–1 μm) rubbery particles dispersed in and bonded to the epoxy network is generated. The toughness of the resulting networks was found to be influenced by the properties of the original functionality of the epoxy resin, the size and volume fraction of the dispersed phase particles, levels of interfacial adhesion, and the properties of the elastomeric modifier[6]. In addition, improvements were observed only for lightly cross-linked epoxies.

Another important aspect of CTBN and amine functionalized butadiene–acrylonitrile copolymer rubbers (ATBN) modified thermoset networks is that the presence of unsaturation (double bonds) in the elastomeric structure provides possible undesirable sites for reaction in oxidative and high-temperature environments. The use of functionally terminated polysiloxanes to chemically modify bisphenol-A-based epoxy resins has also been reported[9]. Siloxane elastomers provide an attractive alternative to the butadiene–acrylonitrile elastomers often used for modification of epoxy networks. Poly(dimethyl siloxane) displays very good thermal stability, good weatherability, oxidative stability and moisture resistance. The non-polar nature and the low surface energy of poly(dimethyl siloxane) constitute a thermodynamic driving force for the siloxane phase to migrate to the air–polymer interface. This is known to occur even in the case of chemically linked microphase-separated systems. Such migration of the siloxane phase leads to the

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formation of a very hydrophobic and chemically bound surface coating. There is evidence to suggest that this 'slippery' surface layer enhances the friction and wear properties of the epoxy substrate[10].

Enhancement of toughness with particulate fillers such as alumina and silica[11], glass[12], dolomite and aluminum hyroxide[11] and zirconia[13] has also been investigated with limited success. Hybrid systems such as glass fillers in rubber-modified epoxies[14] and 'zirconia–rubber–epoxy' systems have also been reported.

The growing demand for tough polymeric materials that display high thermal and dimensional stability led to the concept of thermoplastic-modified thermosets. Toughening studies using commercially non-reactive thermoplastic modifiers[15–18] have not always proved successful, owing possibly to poor adhesion between the substrate and the modifier as well as an unacceptable loss of chemical (solvent) resistance due to the amorphous non-reactive thermoplastic. In our laboratories[19–26] and elsewhere[27] it has been demonstrated that the above-mentioned limitations can be effectively overcome by the incorporation of tough, ductile, functionally terminated, high-T_g thermoplastic modifiers. Improvements in toughness along with retention of the moderately high modulus and thermal stability have been attained in the case of epoxy and bismaleimide networks[19–26].

Cyanate ester resins are bisphenolic[28] or polyphenolic[29] derivatives containing the ring-forming cyanate (–OCN) functional group. Chemically this family of thermosetting monomers and their prepolymers are esters of bisphenol (or polyphenol) and cyanic acid. The esters cyclotrimerize to form substituted triazine rings on heating[28,30]. Cross-linking of cyanate esters occurs via cyclotrimerization (*Figure 1*) to form 3-dimensional networks of oxygen-linked triazine rings. The curing reaction is classified as an addition polymerization and it results in no volatile by-products.

Zeng *et al.*[31] investigated the toughenability of dicyanate matrix composites with particle-modified resin-rich layers. The particles used to modify the resin-rich layers were semicrystalline nylon-6 particles of $20\,\mu$m average diameter. These authors reported that creation of such a layered composite structure resulted in no improvement in 'G_{IC}' but greatly increased 'G_{IIC}.' Yang *et al.*[32,33] investigated the toughenability of the Dow experimental cyanate ester resin XU71787.02 by incorporating an experimental core–shell rubber modifier and reportedly obtained significant enhancements in toughness. They attributed such improvements to a rubber-induced shear yielding mechanism. Arnold *et al.*[34] reported investigations of a number of siloxane-modified cyanates of undisclosed chemistries. The siloxane modifications reportedly resulted in significant improvements in properties such as toughness, microcrack resistance and oxygen plasma resistance over those of the unmodified cyanates. Almen *et al.*[35,36] reported investigations into the use of engineering thermoplastics to toughen cyanates. Although they found significant improvements, the resin chemistries and compositions were not revealed. Some limited work (and the successes obtained) on the thermoplastic modifications of cyanates have also been reported by Shimp *et al.*[37]. Cao *et al.*[38] reported studies of ways to control the morphologies and properties of rubber or thermoplastic-modified cyanates. They examined the phase separation process induced by the step growth polymerization of cyanate ester networks in the presence of elastomeric (butadiene–acrylonitrile random copolymer) or thermoplastic (polyethersulfone) modifiers. Hedrick *et al.*[39] investigated the toughenability of a fluorine-containing polycyanurate thermoset by the incorporation of a reactive, highly compatible engineering thermoplastic. They reported the use of scanning force microscopy (SFM) to confirm the existence of microphase separation.

Research in our laboratories has focused on investigations into the toughenability of bisphenol-A-based cyanate ester networks by the use of a variety of thermoplastic backbone chemistries[40–47]. The role of solubility parameter as a tool for selection of thermoplastic toughener of appropriate backbone chemistry has been reported[40]. Bisphenol-A-[41–43] and phenolphthalein-[44–47] based polyarylene ethers have been used as potential toughness modifiers. We have also reported on the processability of these thermoplastic-modified systems using either thermal or microwave radiation[45,46]. Our earlier work[43] demonstrated that the bisphenol-A-based poly(arylene ether) ketones were effective tougheners for the cyanate ester networks. It was also shown that either hydroxyl or cyanato reactive end-functionalized oligomers could be effectively utilized to toughen the bisphenol-A-based cyanate ester networks. Both were superior to non-reactive modifiers (*t*-butyl phenyl end-functionalized oligomers) in terms of both mechanical performance and solvent stress cracking. For example, in the case of the 15K Bis-A PEK-OH modified networks, fourfold improvements in toughness were observed with a minimal loss in strength and modulus relative to the unmodified networks. However, such improvements were

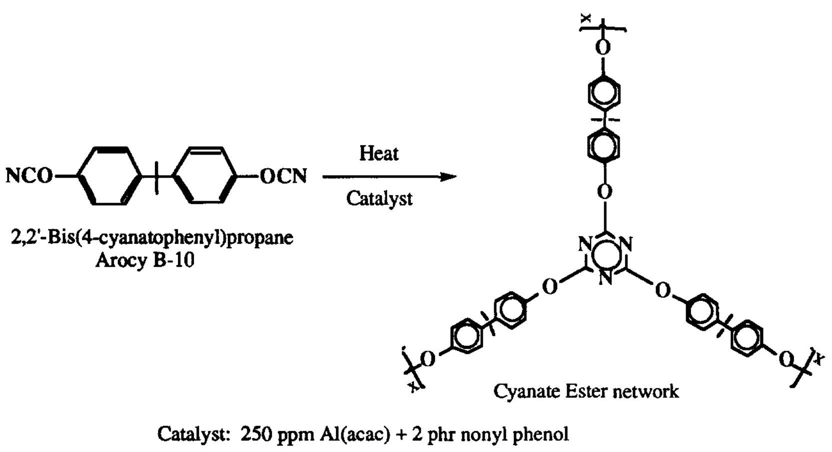


Figure 1 Cyclotrimerization of cyanate esters

accompanied by a significant loss (> 100°C) in terms of 'use temperature'. The use temperature was limited by the 150°C glass transition temperature of the Bis-A PEK-OH oligomers. Phenolphthalein-based polyarylene ethers exhibit significantly higher glass transition temperatures than bisphenol-A-based polyarylene ethers. This led us to investigate the feasibility of tailoring similar toughness improvements (as was demonstrated with the bisphenol-A-based polyarylene ethers) using the phenolphthalein-based poly(arylene ether) backbone chemistry, the premise being that any toughened cyanate ester networks generated in this manner would no longer suffer such serious setbacks in 'use temperature' as was the case with the Bis-A PEK-OH modified networks.

EXPERIMENTAL

Materials

Commercial AroCy B-10 (m.p. 79°C, $d = 1.259$) [2,2'-bis(4-cyanatophenyl)propane], provided by Ciba-Geigy was used as the model thermosetting system. Aluminium acetylacetonate [Al(acac)] (99%) from Strem Chemical and nonylphenol (technical grade) from Aldrich formed the catalyst system used. Phenolphthalein (analytical grade) from Aldrich was recrystallized from methanol (m.p. 261°C). 4,4'-Difluorobenzophenone (DFBP) supplied by AMOCO was recrystallized from toluene. 4,4'-Difluorobenzophenone (DFBP) supplied by ICI was recrystallized from a mixture of ether and petroleum ether. 4,4'-Bis(fluorophenyl)phenyl phosphine oxide (BFPPO) was synthesized in high purity according to a procedure provided by Smith[48]. 4,4'-Bisphenol (m.p. 282–284°C) was recrystallized from a saturated solution in deoxygenated acetone, filtered and vacuum-dried at 100°C. Dimethylacetamide (DMAC) and *N*-methylpyrrolidone (NMP) obtained from Fisher Scientific were distilled under vacuum after stirring with calcium hydride. Potassium carbonate and toluene obtained from Fisher Scientific were used as supplied without further purification.

Synthesis and characterization of thermoplastic oligomers

All oligomers used in this study were synthesized by typical step growth polymerization techniques by co-reacting 'AA' and 'BB' type monomers with or without the presence of a monofunctional end-capper. The stoichiometry of the reaction (molar quantities of the reaction) was dictated by the number-average molecular weight ($\langle M_n \rangle_{\mathrm{theor}}$) that was aimed at. This was facilitated by the use of Carothers' equation; detailed descriptions of the calculations involved are available elsewhere[48,49].

Hydroxyl functionalized phenolphthalein-based amorphous poly(arylene ether ketone) (PPH-PEK-OH)], poly-(arylene ether sulfone) (PPH-PSF-OH) and poly(arylene ether phosphine oxide) (PPH-PEPO-OH) oligomers of controlled molecular weight were synthesized via aromatic nucleophilic substitution, according to the general procedure shown in *Figure 2*[19,29,48–50].

A specific example is outlined for the synthesis of 15K PPH-PSF-OH oligomer. The stoichiometry was also designed to take into consideration the specific type of end-functionality that was required. For example, to synthesize hydroxy functional polyarylene ethers (*Figure 2*), a stoichiometric excess of the bisphenol (depending on the target molecular weight) was taken relative to the dihalide. The apparatus for the synthesis of poly(arylene ether)s involved the use of a 3 L four-neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer and a Dean–Stark trap with a condenser[19,48–51]. Phenolphthalein (250 mmol, 79.5825 g), dichlorodiphenyl sulfone (241 mmol, 69.2859 g) and K_2CO_3 (300 mmol, 41.463 g) were weighed separately on Teflon-coated weighing pans and carefully transferred into the reaction vessel through a powder funnel. The powder funnel was subsequently rinsed several times with DMAC to effect quantitative transfer of reactants into the reaction flask. Then 750 mL DMAC and 200 mL toluene were added to the reaction flask; the ratio of DMAC to toluene used was 70:30. Initially the reaction was conducted at 145–150°C for ~4 h to remove the water azeotropically. Then the temperature was raised to 155–160°C for an additional 12–15 h. A nitrogen atmosphere was continuously maintained in the reaction vessel to prevent oxidative side-reactions. The viscous solution was then filtered free of potassium halide salts as well as unreacted K_2CO_3, neutralized with glacial acetic acid and coagulated into a large excess (5–10 times) of methanol and water (80:20). The polymer was filtered and dried in a vacuum oven. The dried polymer was redissolved in chloroform and recoagulated into excess methanol, filtered and dried in a

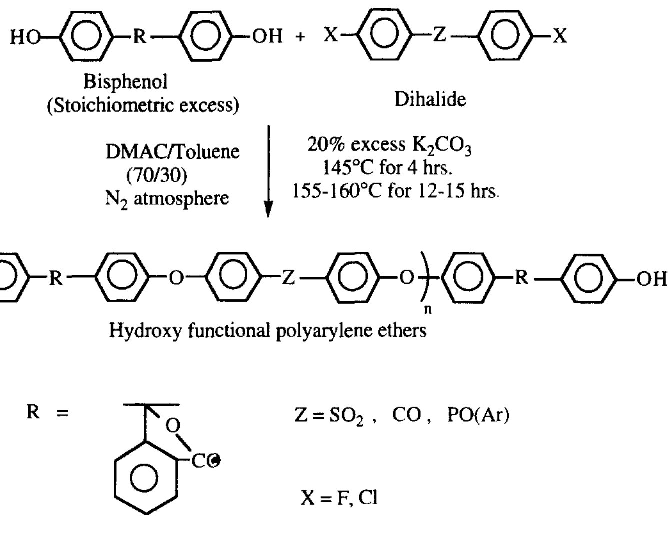
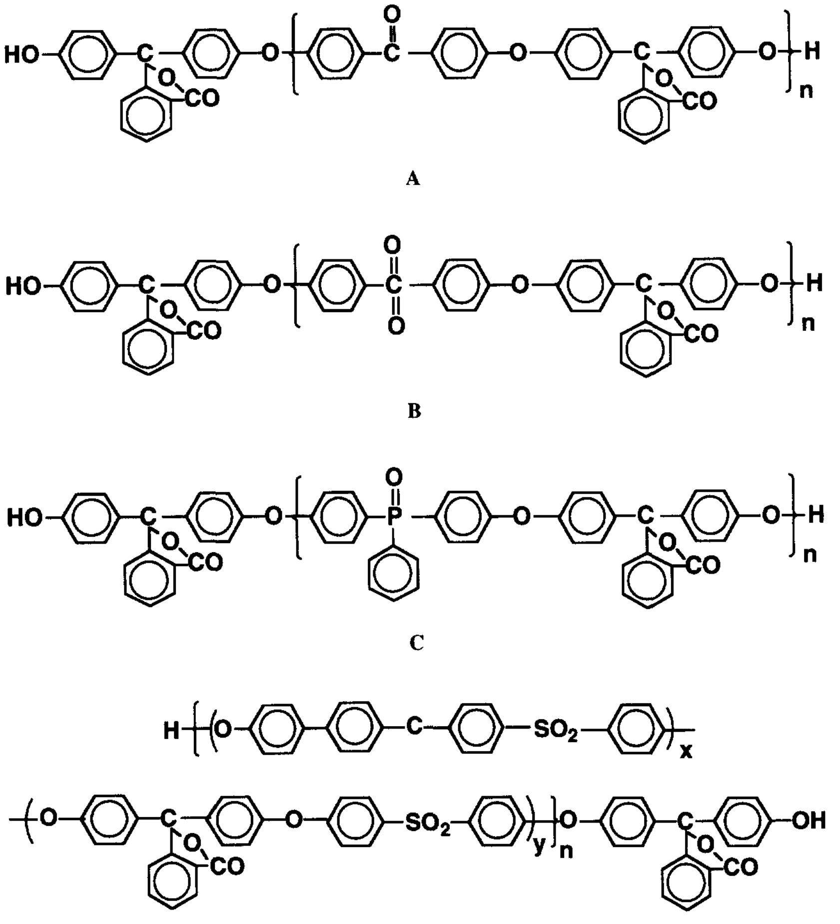


Figure 2 Synthesis of hydroxy functionalized poly(arylene ether)s



A

B

C

D

Figure 3 Hydroxy functionalized phenolphthalein-based poly(arylene ether)s and bisphenol–phenolphthalein statistical copolymer used in this study: (a) hydroxy functionalized poly(arylene ether ketone) (PPH-PEK-OH); (b) hydroxy functionalized poly(arylene ether sulfone) (PPH-PSF-OH); (c) hydroxy functionalized poly(arylene ether phosphine oxide) (PPH-PEPO-OH); (d) hydroxy functionalized 50/50 bisphenol–phenolphthalein statistical polysulfone copolymer (50/50 BP–PPH PSF-OH)

vacuum oven. The thermoplastic structures used are shown in *Figure 3*.

The oligomers were characterized for their end groups, molecular weights and thermal transitions by of titrimetry, measurement of intrinsic viscosity and differential scanning calorimetry (d.s.c.). Intrinsic viscosities or limiting viscosity numbers were measured at 25°C in a Cannon–Ubbelohde viscometer, typically using chloroform as the polymer solvent. Three solutions of low polymer concentration were prepared and the times of passage of the polymer solution (t) and the pure solvent (t_0) through the graduated viscometer path-length were measured. Assuming $t/t_0 = \eta/\eta_0$, the specific viscosity was defined as $\eta_{sp} = (\eta/\eta_0) - 1$ and the reduced viscosity as $\eta_{red} = \ln(\eta/\eta_0)$. Both η_{sp}/c and η_{red}/c were plotted versus concentration c and extrapolated to zero concentration to give the intrinsic viscosity $[\eta]$.

For determination of molecular weight of linear, hydroxy functionalized polyarylene ether oligomers a titration technique[52] was used. An MCI GT-05 automatic titrator (Cosa Instruments) in conjunction with a standard glass-body combination electrode with Ag/AgCl reference electrode was used. The polymer solutions in NMP were titrated against ~0.025N methanolic solution of tetramethylammonium hydroxide (TMAH). The TMAH was standardized by titration against an aqueous solution of potassium hydrogen phthalate (KHP) of known concentration. The procedure involved titrating a solution of a known weight (w) of the polymer in NMP versus TMAH of standardized normality (N). M_n was estimated using the formula $M_n = (200w)/(N \times (B - Bl))$, where B represents the volume of TMAH consumed by the polymer solution and Bl represents the blank titration value. With P_i and P_e representing the initial and endpoint millivolt potentials of the actual titration profile, the blank titration value was estimated as the amount of titrant used by the NMP alone over the potential change ($P_e - P_i$). $\langle M_n \rangle$ was estimated as an average of three or four different titrations for each molecular weight.

Differential scanning calorimetry (d.s.c.) was performed on a DuPont 912 instrument. The glass transition temperatures (T_g) reported were obtained on samples that had been cold-pressed and secured in crimped aluminium pans. Scans for amorphous polymers were performed by heating at 10°C min^{-1} to $T > T_g$, quenching to room temperature and re-scanning at 10°C min^{-1}. The T_g values reported are those from the second scans.

Preparation and characterization of hot-melt blends of cyanate ester resin with thermoplastic modifiers

The amorphous polymers were dissolved in molten AroCy B-10 cyanate precursors at 90–100°C to obtain a homogeneous melt. The melt was vacuum-treated to remove any volatiles or entrapped air. As soon as degassing was complete, the catalyst (250 ppmw Al(acac) + 2 ppmw nonylphenol) was added with stirring and the reaction mixture was further degassed. The hot resin was subsequently poured into preheated (100°C) silicone rubber moulds for fracture toughness (K_{IC}) and tensile dogbone and dynamic mechanical analysis (DMA) specimens. The melts were then cured using an optimized cure protocol of 3 h–104°C, 1 h–200°C and 2 h–250°C, with subsequent slow cooling (1–2°C min^{-1}), unless otherwise specified. Gel fractions were determined by Soxhlet extraction with cloroform for 3 days, followed by vacuum drying. The postulated chemical processes leading to three-dimensional insoluble networks are represented in *Figure 1*[28,30,53,54].

Infrared spectroscopic measurements were performed on a Nicolet-800 *FT*i.r. spectrophotometer, using thin films of the resin coated on to an NaCl salt plate. Dynamic mechanical analysis (DMA) was performed on a Perkin-Elmer DMA-7 analyser in the three-point bending mode. Tests were conducted at a frequency of 1 Hz with a dynamic temperature scan rate of 3°C min^{-1}. Dynamic mechanical thermal analysis (DMTA) was performed on a Polymer Laboratories DMTA analyser in the bending mode. Tests were conducted at multiple frequencies with a dynamic temperature scan rate. Fracture toughness (K_{IC}) measurements were conducted in accordance with ASTM D5045-91 (E399-90) test method on 10–12 specimens of dimensions 3.2 × 6.5 × 38 mm. The samples were notched at the centre to a depth of ~0.5 mm using a reciprocating saw. Sharp cracks were then initiated with a fresh surface of liquid-nitrogen-cooled razor blade and tapping the sharp blade within the notch. Care was taken to ensure that the crack had propagated evenly through the specimen thickness. The precracked specimens were then loaded on a three-point bend fixture attached to an Instron machine and tested at a rate of 1.27 mm min^{-1}. Stress–strain measurements were performed in accordance with ASTM D638 (Sample-V), using a crosshead speed of 1.27 mm min^{-1}. An average of four to five samples were tested for each measurement. Morphologies of the fractures surface were determined by scanning electron microscopy using an International Scientific Instruments Model SX-40. Samples were mounted on aluminium substrates with silver paint and the fracture surfaces were sputter-coated with a ~10 nm gold film using a Bio Rad Polaron (Model E 4500) sputter coater. Scanning transmission electron microscopy (STEM) was performed on microtomed thin sections of samples stained with ruthenium oxide. Analyses were performed on a Philips 420T electron microscope utilizing a backscattering detector.

RESULTS AND DISCUSSION

The results of the characterization of the hydroxyl functionalized phenolphthalein-based amorphous poly(arylene ether ketone) (PPH-PEK-OH), poly(arylene ether sulfone) (PPH-PSF-OH) and poly(arylene ether phosphine oxide) (PPH-PEPO-OH) oligomers are given in *Table 1*.

All comparisons with respect to properties such as tensile properties, fracture toughness etc. have been made relative to the unmodified fully cured network. This required that any cure cycle used in this study should result in a fully cured network. The cure cycle most commonly used in this study was 3 h–104°C, 1 h–200°C, 2 h–250°C, with a heating rate of 4–5°C min^{-1} between steps. The catalyst/co-catalyst concentration was kept constant at 250 ppmw Al(acac) in 2 phr nonylphenol. The extent of reaction attained with such a cure cycle was estimated by *FT*i.r. to be > 99%. The decrease in peak height due to the 2270 cm^{-1} C–N stretch was ratioed relative to the C–H stretch of the isopropylidene group which was used as the reference. Additionally, in any modification of the above cure cycle that was used, the final stage always involved a 2 h–250°C cure. This ensured that the networks in all cases were fully cured (> 99% gel fraction, as judged by Soxhlet extraction with chloroform). The unmodified cured networks had a T_g of 265–270°C as detected by DMA at a frequency of 1 Hz.

Effect of backbone chemistry

DMA analyses (*Figure 4*) on 15K PPH-PSF-OH modified networks exhibited a single peak of decreasing intensity with increasing loadings from 0 to 30 wt% modifier. The 15K PPH-PEPO-OH modified networks (*Figure 5*) also exhibited a single peak, but shifted to lower temperatures

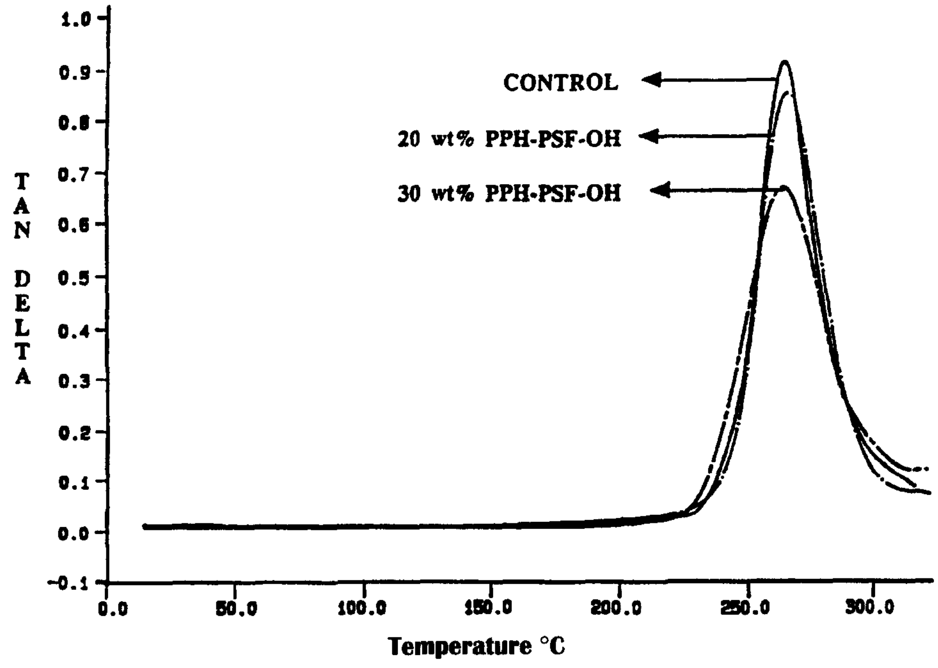


Figure 4 DMA spectrum showing tan δ as a function of temperature (°C) at a frequency of 1 Hz for the 15K PPH-PSF-OH modified networks

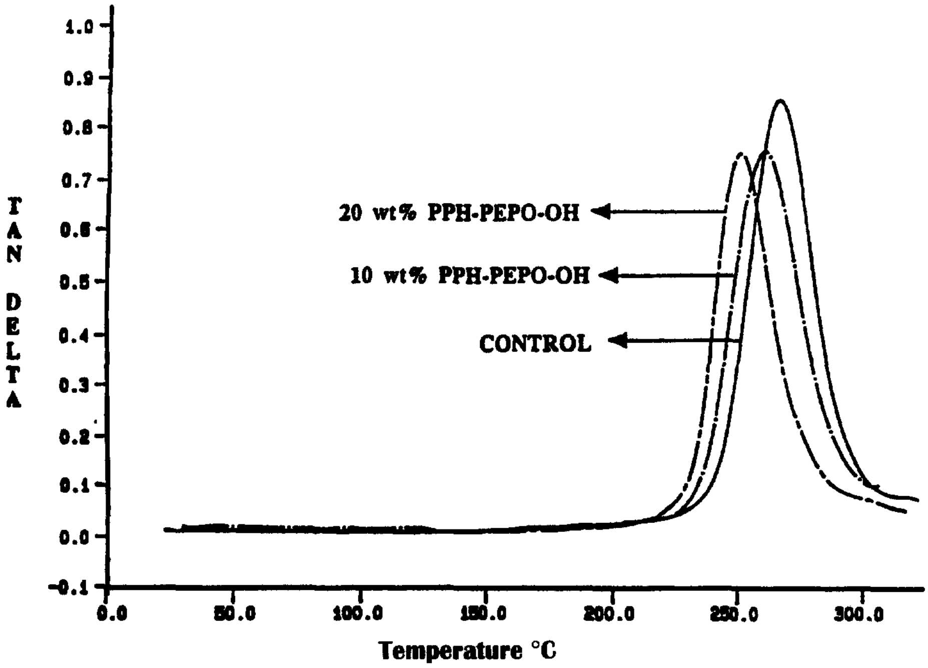


Figure 5 DMA spectrum showing tan δ as a function of temperature (°C) at a frequency of 1 Hz for the 15K PPH-PEPO-OH modified networks

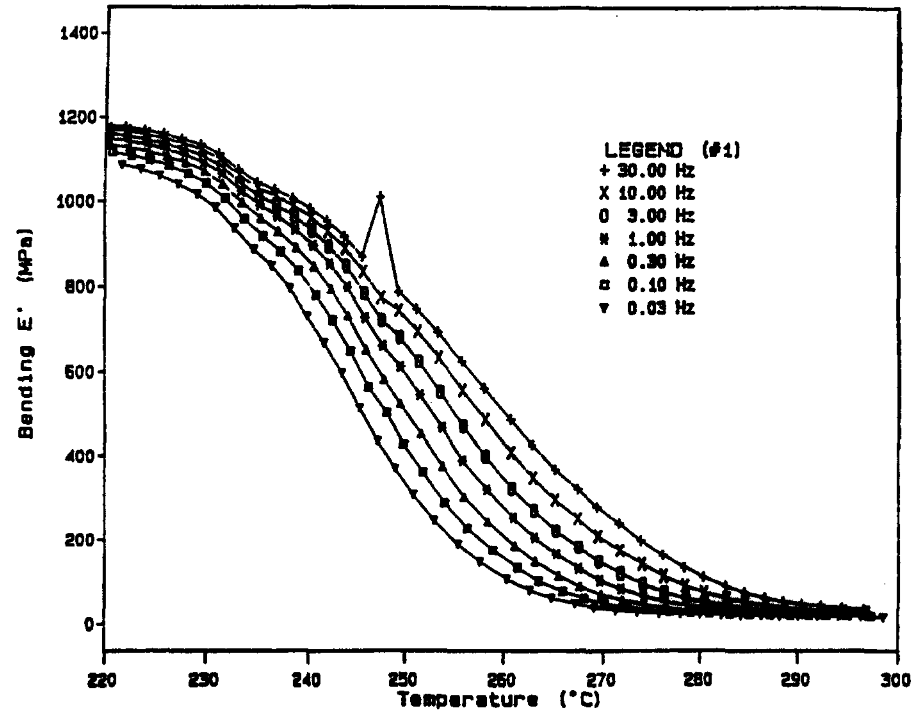


Figure 6 DMTA spectrum showing bending modulus (E') as a function of temperature (°C) at a frequency of 0.03–30 Hz for the 30 wt% 15K PPH-PSF-OH modified networks

Table 1 Solution and thermal characterization of hydroxy functional phenolphthalein-based poly(arylene ether)s and 50/50 biphenol–phenolphthalein statistical polysulfone copolymers

Polymer type	Theoretical $\langle M_n \rangle$ (g mol^{-1})	$[\eta]^a$, 25°C (dL g^{-1})	$\langle M_n \rangle^b$, titration (g mol^{-1})	T_g^c, 10°C min^{-1} (°C)
PPH-PSF-OH	10K	0.18	8900	252
PPH-PSF-OH	15K	0.26	15 500	259
PPH-PSF-OH	20K	0.33	21 050	262
PPH-PEPO-OH	15K	0.29	15 100	265
PPH-PEK-OH	15K	0.32	16 000	226
BP–PPH-PSF-OH	16K	0.31	15 800	242

[a] In $CHCl_3$
[b] Titration of phenolic end-groups with 0.025N tetramethylammonium hydroxide
[c] D.s.c. 10°C min^{-1}

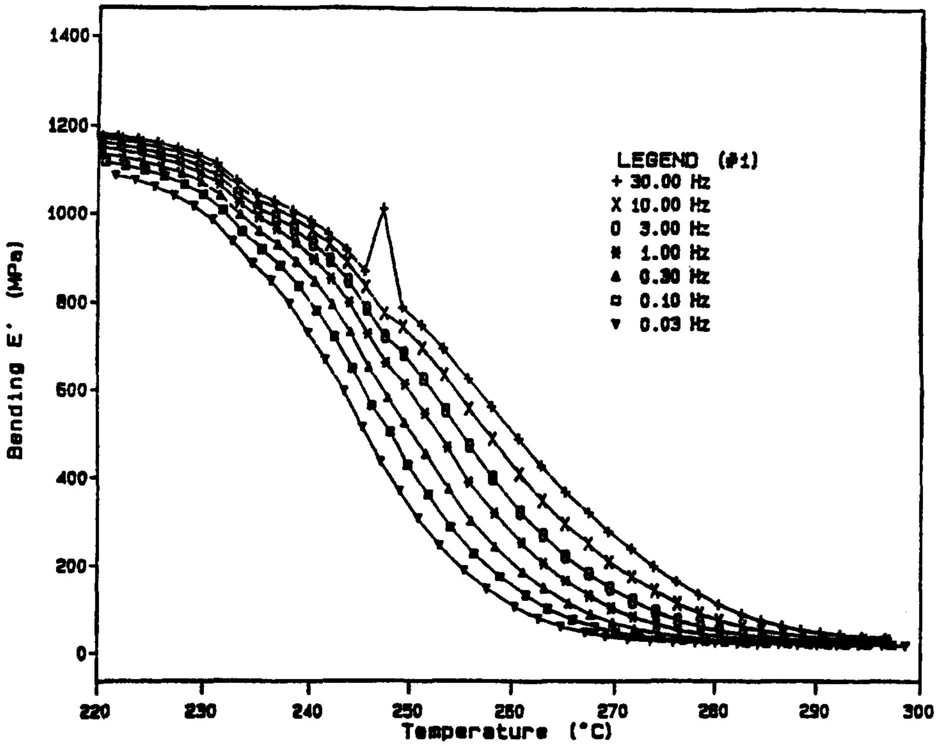


Figure 7 DMTA spectrum showing tan δ as a function of temperature (°C) at a frequency of 0.03–30 Hz for the 30 wt% 15K PPH-PSF-OH modified networks

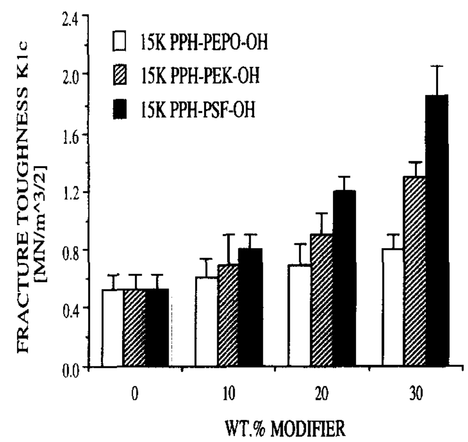


Figure 8 Fracture toughness K_{IC} (MN m$^{-3/2}$) as a function of phenolphthalein-based poly(arylene ether) concentration

with increasing loading. From *Table 1* it is seen that the glass transition temperatures of the PPH-PSF-OH and PPH-PEO-OH oligomers are in the range 260–265°C. These values are in close proximity to the glass transition temperature (~265–270°C) of the unmodified cured cyanate ester networks as detected by DMA at a frequency of 1 Hz. Accordingly, it is difficult to confirm the presence or absence of multiple phases in *Figures 4 and 5*. An examination of *Figures 4 and 5* suggests the possibility that the 15K PPH-PEPO-OH modified networks are relatively more phase-mixed than the 15K PPH-PSF-OH modified networks. This aspect is further corroborated by STEM analysis, as will be discussed later.

The presence of multiple phases in the 15K PPH-PSF-OH polysulfone modified networks was confirmed by 1°C min^{-1} DMTA (*Figure 6*) scans at frequencies ranging from 0.03 to 30 Hz. The modulus–temperature plot clearly shows the presence of multiple phases, corresponding to the dips in the curves. However, the presence of multiple phases is not readily apparent in the tan δ–temperature plots, as seen in *Figure 7*.

Figure 8 shows the fracture toughness trends as a function of thermoplastic backbone chemistry for the $\langle M_n \rangle$ ~15K phenolphthalein-based poly(arylene ether) oligomers. Significant improvements were observed in the case of the PPH-PSF-OH polysulfone modified networks, whereas even with 30 wt% loadings of 15 K PPH-PEPO-OH phosphine oxide only marginal improvements resulted. The fracture toughness values in the case of the 15K PPH-PEK-OH modified networks were found to be intermediate between those of the 15K PPH-PSF-OH and the 15K PPH-PEPO-OH modified networks. Such trends in fracture toughness correlate well with the extents of deformation and texture evidenced in the fracture surface micrographs.

Improvements in fracture toughness were observed only in those modified networks where sufficient texture was further revealed by the fracture surface analysis. The smooth and textureless fracture surfaces (*Figure 9*) of the 15K PPH-PEPO-OH modified networks translated into relatively negligible improvements in fracture toughness (K_{IC}) relative to the unmodified networks. In contrast, the fracture surfaces of the PPH-PSF-OH modified networks (*Figure 10*) exhibited extensive deformation and consequently much higher fracture toughness. However, the morphological features of the modified networks were not readily apparent from an examination of the fracture surface micrographs.

Further investigations of the morphological features of these systems were carried out by STEM analysis of RuO_4-stained microtomed thin sections. The STEM analysis of the 15K PPH-PSF-OH modified networks is represented in *Figure 11*. The dark stained regions correspond to the thermoplastic domains. At 10 wt% loading of 15K

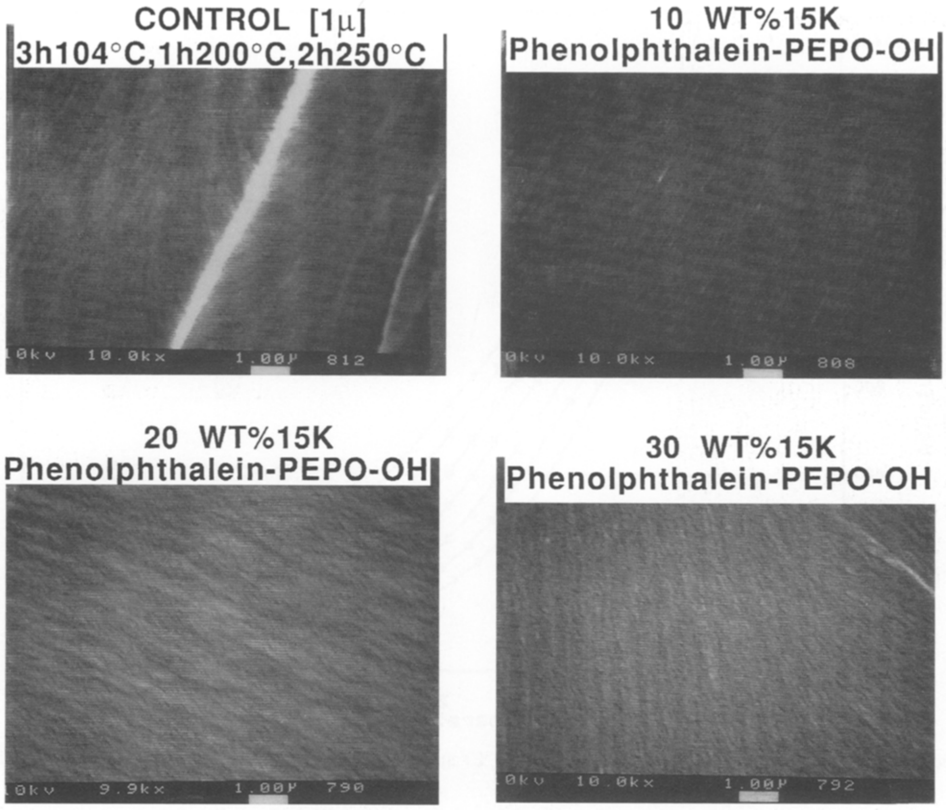


Figure 9 SEM of fracture surfaces of 15K PPH-PEPO-OH modified cyanate ester networks

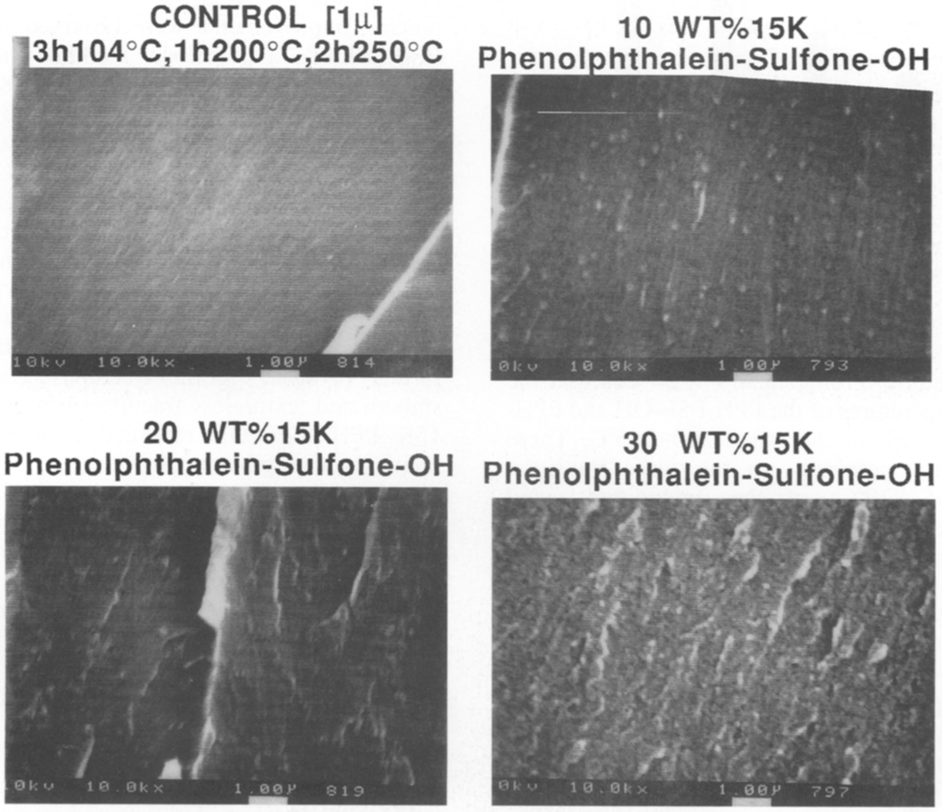


Figure 10 SEM of fracture surfaces of 15K PPH-PSF-OH modified cyanate ester networks

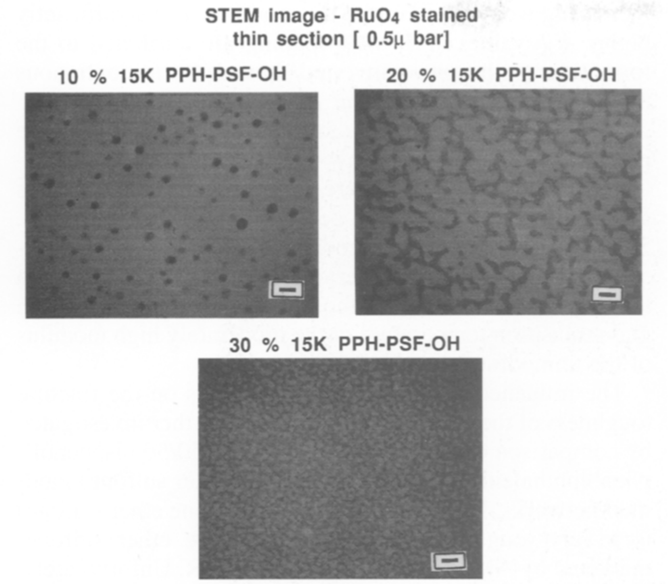


Figure 11 STEM micrographs of RuO_4-stained thin sections of 15K PPH-PSF-OH modified networks

PPH-PSF-OH, the morphology is essentially a continuous phase of the cyanate ester with a dispersed phase of the thermoplastic. A 20 wt% loading of the thermoplastic results in a typical co-continuous type of morphological structure. A 30 wt% loading of the thermoplastic results in a phase-inverted morphology in which the thermoplastic is now the continuous phase with a dispersed phase of the cyanate ester thermoset. STEM analysis of RuO_4-stained microtomed thin sections of the 15K PPH-PEPO-OH modified networks did not indicate any preferential staining, suggesting that these networks are phase-mixed compared with the 15K PPH-PSF-OH modified networks.

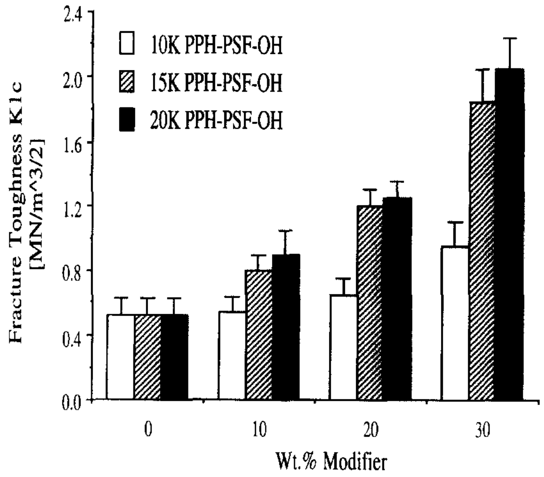


Figure 12 Fracture toughness K_{IC} ($MN\,m^{-3/2}$) as a function of phenolphthalein-based poly(arylene ether sulfone) concentration: effect of molecular weight

Effect of molecular weight

Figure 12 indicates the increase in fracture toughness with increasing molecular weight of the PPH-PSF-OH modifier. The insignificant improvements in fracture toughness values observed for the 10K PPH-PSF-OH modified networks is further reflected by the absence of texture in the fracture surface (*Figure 13*). In fact, the presence of multiple phases was not evidenced in these samples even by STEM analysis (*Figure 14*). This suggests

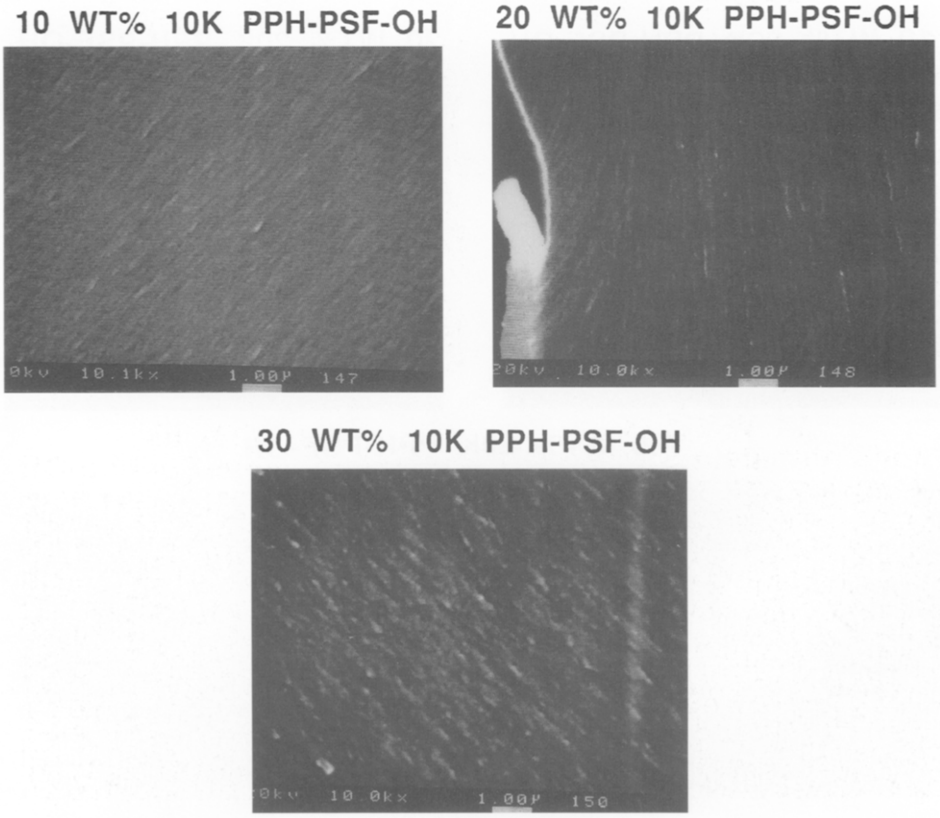


Figure 13 SEM of fracture surfaces of 10K PPH-PSF-OH modified cyanate ester networks

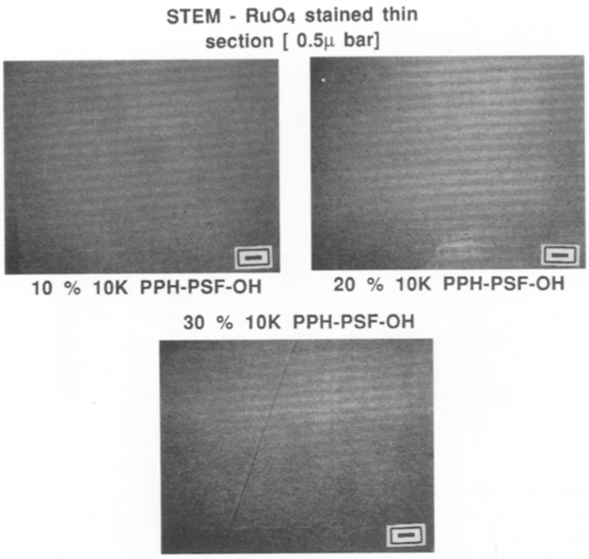


Figure 14 STEM micrographs of RuO_4-stained thin sections of 10K PPH-PSF-OH modified networks

that it is essential to tailor both the backbone chemistry and the molecular weight of the thermoplastic modifier in efforts to control the sizes of the phase-separated domains. The sizes of the phase-separated domains in turn control the fracture toughness of the modified networks. Increasing the molecular weight of the PPH-PSF-OH modifier to 20K (*Figure 12*) resulted in much better improvements in fracture toughness relative to the 15K PPH-PSF-OH modified networks. This was attributed to the larger sizes of the phase-separated domains, as illustrated in *Figures 15 and 16*. In general, the fracture toughness (*Figure 12*) increased with both increasing molecular weight and increasing weight per cent of the modifier. The significantly higher K_{IC} values at 30 wt% loading are attributed to the formation of the phase-inverted thermoplastic continuous morphology (*Figures 11, and 16*).

Preliminary investigation of room-temperature tensile properties suggest that at 30 wt% loading of 15K PPH-PSF-OH, a roughly fourfold increase in fracture toughness is accompanied by only a 10% decrease in modulus (*Table 2*). Since the unmodified and modified networks have comparable glass transition temperatures, the improvements in toughness were attained without sacrificing either the high glass transition temperature or the moderately high modulus of the unmodified cyanate ester networks.

The influence of morphological features on the fracture toughness of the resulting networks was further investigated by comparison of 15K PPH-PSF-OH and 50/50 bisphenol–phenolphthalein-based co-poly(arylene ether sulfone) modified networks. Bisphenol-based poly(arylene ether sulfone) is a very tough commercial poly(arylene ether sulfone) marketed by AMOCO Chemical as Radel R. Unfortunately, it undergoes solvent-induced crystallization. It is essential that the thermoplastic modifier should dissolve completely in the thermosetting resin precursor before being cross-linked. Obviously, amorphous thermoplastics are preferred to semicrystalline ones. A 50/50 amorphous copolymer based on bisphenol and phenolphthalein (Scheme 3) was synthesized for further investigation as a potential

Table 2 Tensile properties of 15K PPH-PSF-OH modified networks

Modifier (wt%)	Modulus (GPa)	Strength (MPa)	Strain at break (%)
0	3.17 ± 0.14	86.2 ± 6.9	2.5
10	3.19 ± 0.07	86.2 ± 3.4	2.5
20	3.10 ± 0.09	75.8 ± 8.3	3.2
30	2.90 ± 0.13	69.0 ± 5.5	4.0

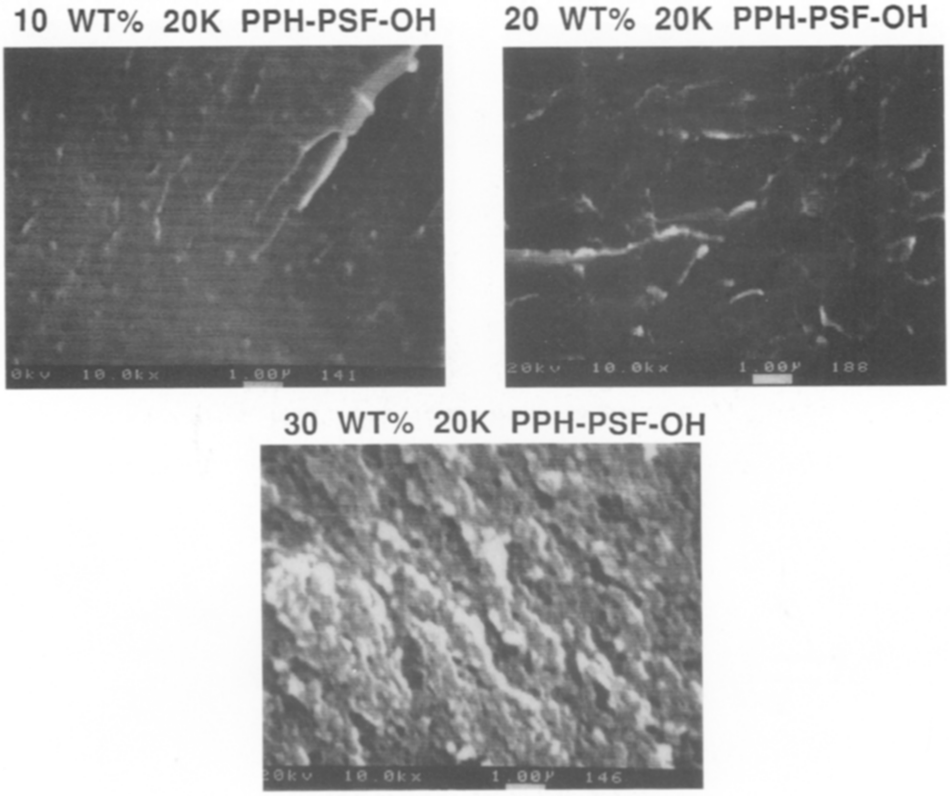


Figure 15 SEM of fracture surfaces of 20K PPH-PSF-OH modified cyanate ester networks

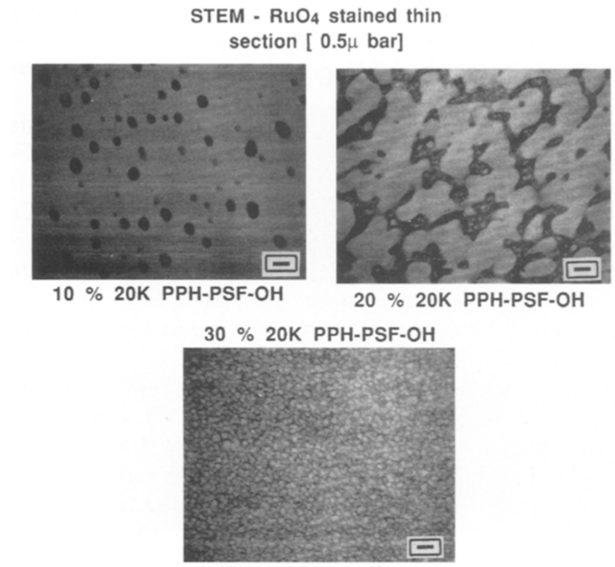


Figure 16 STEM micrographs of RuO_4-stained thin sections of 20K PPH-PSF-OH modified networks

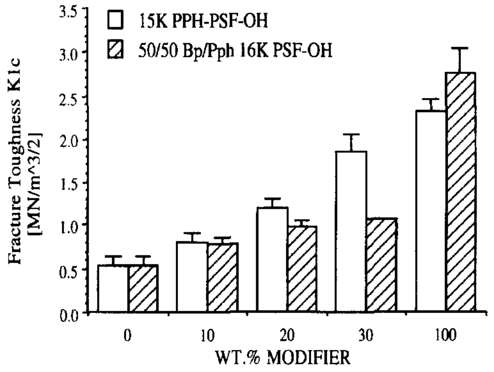


Figure 17 Fracture toughness K_{IC} ($MN\,m^{-3/2}$) as a function of poly(arylene ether sulfone) concentration of modified cyanate ester networks

toughness modifier, and some characterization of this copolymer is provided in *Table 1*.

Comparative trends in fracture toughness between the 15K PPH-PSF-OH and 16K 50/50 BP–PPH PSF-OH modified networks are shown in *Figure 17*. Although the bisphenol–phenolphthalein-based copolymer is intrinsically tougher than the phenolphthalein-based poly(arylene ether sulfone) as expected, the 15K PPH-PSF-OH modified networks exhibit higher fracture toughness values than those of the 16K 50/50 BP–PPH PSF-OH modified networks. This is probably due to the relative sizes of the microphase-separated domains. For example, *Figure 18* shows STEM micrographs of microtomed thin sections where the stained regions correspond to the thermoplastic phase. In comparison with the 15K PPH-PSF-OH modified networks (*Figure 11*), it is seen that the domain sizes of the 16K 50/50 BP–PPH PSF-OH copolymer modified networks (*Figure 18*) are considerably smaller. Moreover, smooth textureless fracture surfaces are observed, as shown in *Figure 19*. However, it should be mentioned that the presence of multiple phases that were elucidated by staining techniques (*Figure 18*) was not detected by DMTA analysis (*Figure 20*).

CONCLUSIONS

Controlled molecular weight (10–20K) quantitatively hydroxyl functional homopolymer phenolphthalein-based poly(arylene ether ketone)s, poly(arylene ether sulfone)s and poly(arylene ether phosphine oxide)s, as well as a hydroxy functional 50/50 co-poly(arylene ether sulfone) based on bisphenol and phenolphthalein were synthesized and characterized. The functionalized amorphous oligomers were soluble in and subsequently co-cured with commercially available bisphenol-A-based cyanate ester resins, to generate thermoplastic modified networks.

The use of hydroxyl functionalized phenolphthalein-based amorphous poly(arylene ether sulfone) modifiers resulted in remarkable improvements in the toughness of

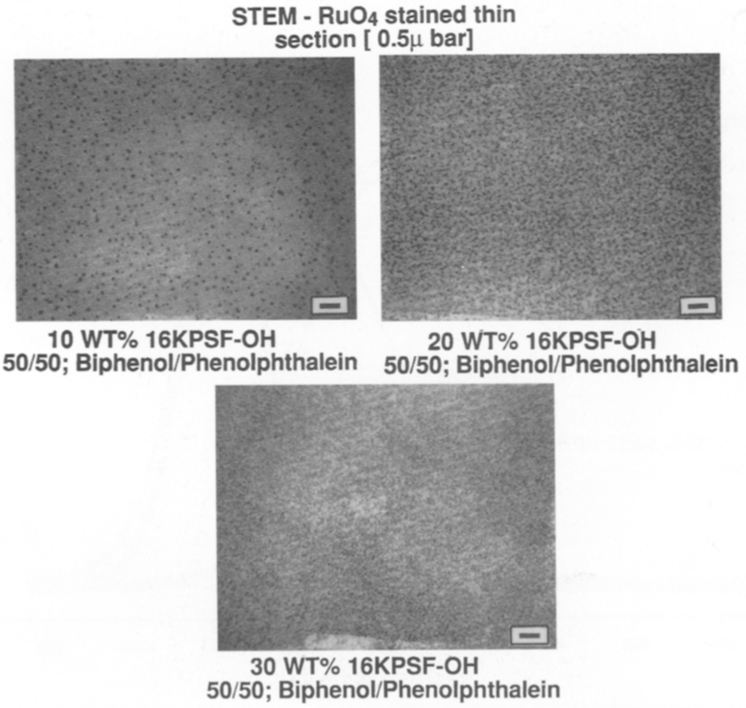
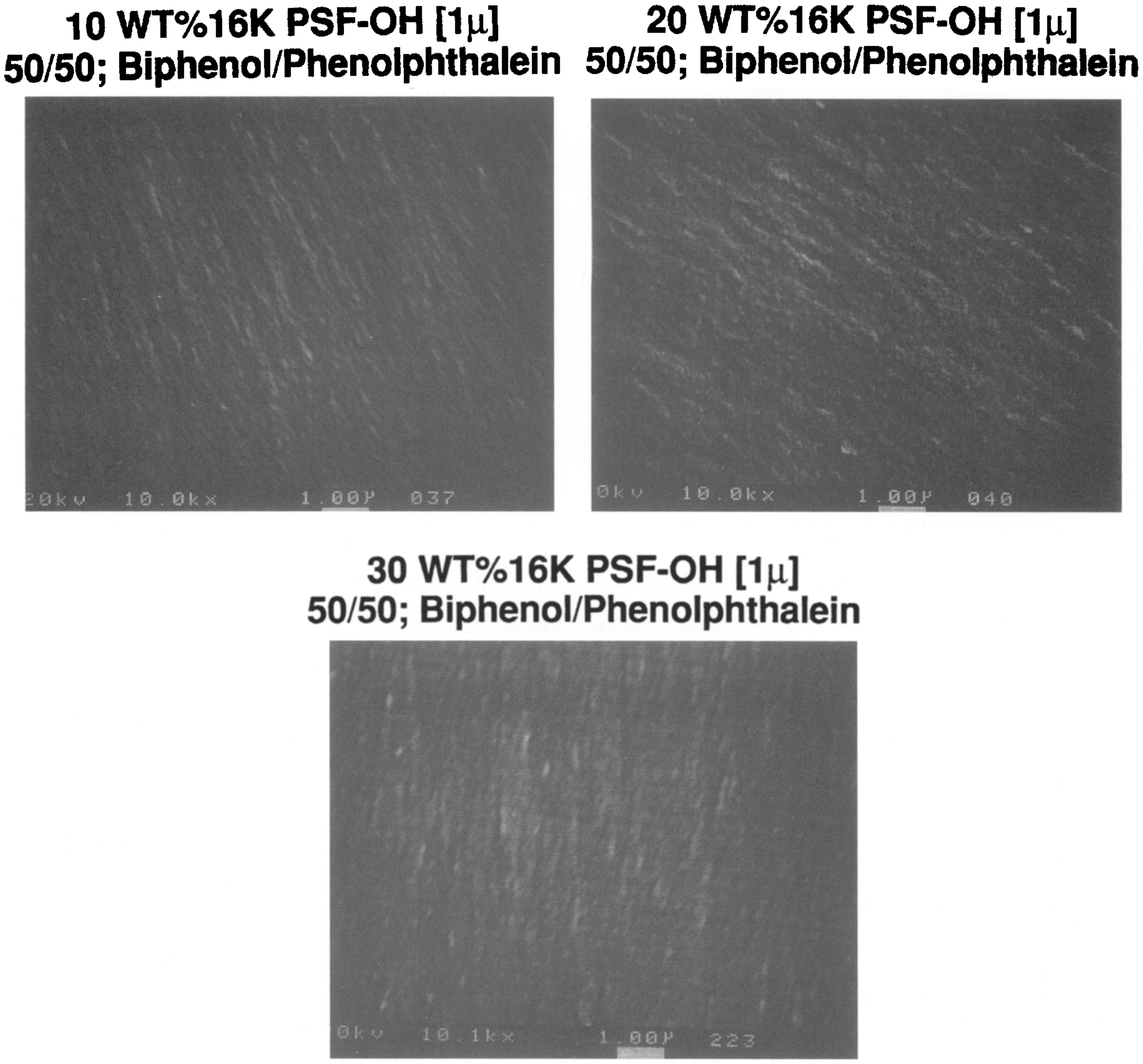


Figure 18 STEM micrographs of RuO_4-stained thin sections of 16K 50/50 BP–PPH PSF-OH modified networks



10 WT%16K PSF-OH [1μ]
50/50; Biphenol/Phenolphthalein

20 WT%16K PSF-OH [1μ]
50/50; Biphenol/Phenolphthalein

30 WT%16K PSF-OH [1μ]
50/50; Biphenol/Phenolphthalein

Figure 19 SEM of fracture surfaces of amorphous 16K 50/50 BP–PPH PSF-OH modified networks

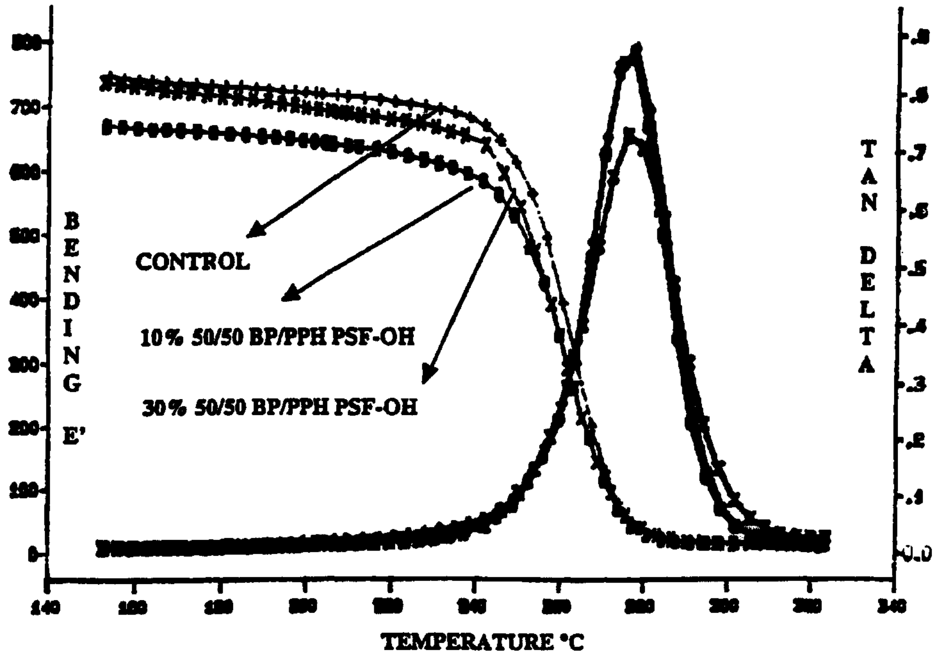


Figure 20 DMTA spectra showing bending modulus (E') and tan δ as a function of temperature (°C) at 3°C min^{-1} and a frequency of 1 Hz for the 16K 50/50 BP–PPH PSF-OH modified networks

cyanate ester networks. Toughened multiphase networks were generated without sacrificing either the T_g or the moderately high modulus of the unmodified cyanate ester networks. The toughenability of these thermoplastic-modified systems depended on the formation of microphase-separated morphology and the sizes of the phase-separated domains. Phosphine oxide modifiers were more homogeneous and thus the backbone chemistry and the molecular weight of the thermoplastic modifier were determined to be key factors in influencing the heterophase morphological structure. Some complementary research has also been recently published[55,56].

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