

Amorphous Phenolphthalein-Based Poly(arylene ether)-Modified Cyanate Ester Networks: Microwave Processing

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ABSTRACT: Toughenability of cyanate ester networks with reactive hydroxyl-functionalized phenolphthalein-based amorphous poly(arylene ether sulfone) thermoplastics, via conventional thermal curing, without a sacrifice in either the T_g or the moderately high modulus of the unmodified cyanate ester networks was already demonstrated. The present article investigated the rapid processing of unmodified and thermoplastic-modified cyanate ester networks utilizing microwave radiation. Controlled morphologies were generated by variations in both the rates of conversion and the thermoplastic compositions. Improved toughness can be achieved which can be coupled with significantly reduced curing times. The use of nonreactive modifiers resulted in macrophase separation in contrast to the well-defined morphologies of the reactive thermoplastic-modified networks. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 179–190, 1997

INTRODUCTION

Conventionally, thermoset crosslinking is carried out employing thermal energy. In our laboratories, it was demonstrated that microwave radiation can be effectively utilized to process reactive thermosetting polymers.^{1–3} Interactions of microwave radiation with various polymeric materials were also studied.⁴ In contrast to conventional thermal cure (processing time is a few hours), the use of microwave radiation (processing time scale is in minutes) to process thermosetting materials has the potential advantage of significantly reduced cure times as well as producing materials that may display lower residual stresses.⁵ In addition, the microwave-cured networks exhibit comparable mechanical properties and improvements in thermal and adhesive properties relative to thermally cured networks.³ Novel morphologies

were also reported in the case of thermoplastic-modified epoxies and bismaleimides that were cured employing microwave radiation and this was attributed to the accelerated cure resulting probably due to a more efficient energy transfer.¹ Microwave heating of materials takes place via dielectric power absorption and is described by eq. (1):

$$P = KfE^2\varepsilon' \tan \delta \quad (1)$$

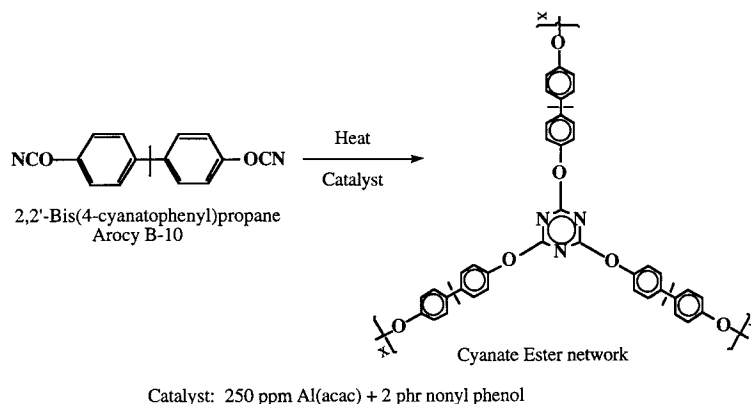
where P is the power dissipation in W/cm^3 ; K , a constant equal to 55.61×10^{-14} ; f , the applied frequency in Hz; E , the electric field strength in V/cm ; ε' , the dielectric constant; and $\tan \delta$, the dielectric loss tangent. Both ε' and $\tan \delta$ depend upon the frequency and the sample temperature. The electromagnetic field energy dissipated as heat per unit volume is proportional to the dielectric loss factor ($\varepsilon' \tan \delta$), the square of the field strength E^2 , and the frequency (f) of the applied field. Polarization in homogeneous dielectric materials may be classified into three categories based on their atomic or molecular origins, viz. “electronic,” “atomic,” and “dipolar” polarization.

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Scheme 1 Cyclotrimerization of cyanate esters.

The mechanism of energy transfer in microwave heating is postulated to occur by electric dipolar coupling of the radiation to permanent dipole moments in the polymer, rather than by thermal conductivity as in conventional processing. The degree of polarization of molecules and the energy required to achieve it control the loss factor or dissipation factor of a material. A material that is readily polarized by a small electric field has a high loss factor and, consequently, is easier to heat. The dielectric loss factor, ϵ'' , primarily determines the rate of conversion of electrical energy into thermal energy in the material before phase transition losses. As the electromagnetic field penetrates the bulk material, heat is generated. Thus, until conduction and convection heat losses become important, the dielectric power dissipation is independent of the heat flow through the surface of the material. This is in contrast to conventional thermal heating which is dependent on the thermal conductivity of the material and is therefore much more time-consuming.

Cyanate ester or triazine networks are important candidates for high-temperature adhesives and composite matrix applications. The dicyanate ester monomers cyclotrimerize^{6–8} via addition polymerization to form highly crosslinked polycyanurates (Scheme 1).

Low toughness is a major drawback with most tightly crosslinked materials, including the cyanate ester networks. Attempts have been made at improving the toughness of cyanate ester networks and their fiber-reinforced composites (based on cyanate ester as the matrix resin). These include modifications with siloxanes⁹ and engineering thermoplastics.^{10,11} Research in our laboratories has sought to further advance this general study by focusing on modifications of a

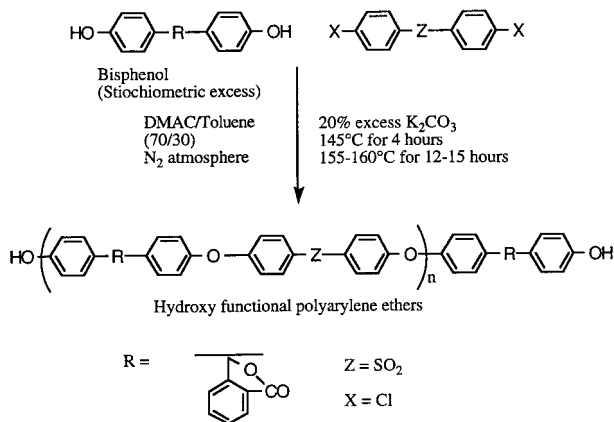
specific cyanate ester network system based on bisphenol A (AroCy B-10) with thermoplastic modifiers of tailored backbone chemistry, backbone molecular weight, and end-group functionality. In particular, hydroxyl-functional phenolphthalein-based amorphous poly(arylene ether sulfone)s ($T_g \sim 265^\circ\text{C}$) had been successfully utilized to toughen the cyanate ester networks ($T_g \sim 265\text{--}270^\circ\text{C}$).^{12,13} This was significant in that toughened multiphase networks were generated without sacrifice in either the T_g or the moderately high modulus of the unmodified cyanate ester networks.^{12,13} The toughenability of the networks was shown to be strongly influenced by the intrinsic toughness of the thermoplastic modifier and the formation of microphase-separated morphologies.

The objective of this part of the research was to investigate the feasibility of processing the 15K hydroxy-functionalized phenolphthalein-based poly(arylene ether sulfone)-modified cyanate ester networks utilizing microwave radiation. These investigations focused on the feasibility of processing the thermoplastic-modified cyanates with microwave radiation, in addition to generating varied morphologies, as was done with the thermal cure. The possibility of generating-controlled morphologies by variations in the rates of conversion and thermoplastic compositions was investigated.

EXPERIMENTAL

Materials

Commercial Arocy B-10 [mp 79°C , $d = 1.259$, 2,2'-bis(4-cyanatophenyl)propane], provided by Ciba-



Scheme 2 Synthesis of hydroxy functionalized poly(arylene ether)s.

Geigy, was utilized as the model thermosetting system. Aluminum acetylacetonate [$Al(acac)$] (99%) from Strem Chemicals and nonyl phenol (technical grade) from Aldrich constituted the catalyst system that was employed. Phenolphthalein (analytical grade) from Aldrich was recrystallized from *methanol* (mp 261°C). 4-*tert*-Butylphenol was obtained from Aldrich and sublimed prior to use. 4,4'-Dichlorodiphenylsulfone (DCDPS) supplied by AMOCO was recrystallized from toluene. 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

Hydroxyl-functionalized phenolphthalein-based amorphous poly(arylene ether sulfone) (PPH-PSF-OH) oligomers of controlled molecular weight were synthesized via aromatic nucleophilic substitution, according to the general procedure provided in Scheme 2. Tertiary-butylphenyl-functionalized phenolphthalein-based amorphous poly(arylene ether sulfone) (PPH-PSF-*t*Bu) oligomers were synthesized according to the general procedure provided in Scheme 3.

A specific example is outlined for the synthesis of 1 15,000 (M_n) (15K) PPH-PSF-*t*Bu oligomer. The stoichiometry was also designed to take into consideration the specific type of end-functionality that was required. For example, to synthesize

tert-butylphenyl functional poly(arylene ether)s (Scheme 3), a stoichiometric amount of a mono-functional endcapper (*t*-butylphenol) was employed, depending on the target molecular weight. 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. Phenolphthalein (241 mmol, 76.7589 g), dichlorodiphenylsulfone (250 mmol, 71.79 g), *t*-butylphenol (17.7 mmol, 2.663 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 a 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 approximately 4 h to azeotrope off the water. Then, the temperature was increased to 155–160°C for an additional 12–15 h. A nitrogen purge was continuously maintained within 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 reprecipitated into excess methanol, filtered, and dried in a vacuum oven. The thermoplastic structures employed are shown in Scheme 4.

Phenolphthalein-based Poly(arylene ether) Thermoplastic Toughness Modifiers

The oligomers were characterized for their end groups, molecular weights, and thermal transitions by means of intrinsic viscosities, titrimetry, nuclear magnetic resonance (NMR) spectroscopy, and differential scanning calorimetric (DSC) analyses. Intrinsic viscosities were measured at 25°C in a Cannon-Ubbelohde viscometer, typically using chloroform as the polymer solvent. To determine the molecular weight of hydroxy-functionalized poly(arylene ether) oligomers, a titration technique was utilized. An MCI GT-05 automatic titrator (Cosa Instruments Corp.) in conjunction with a standard glass-body combination electrode with a Ag/AgCl reference electrode was used. The

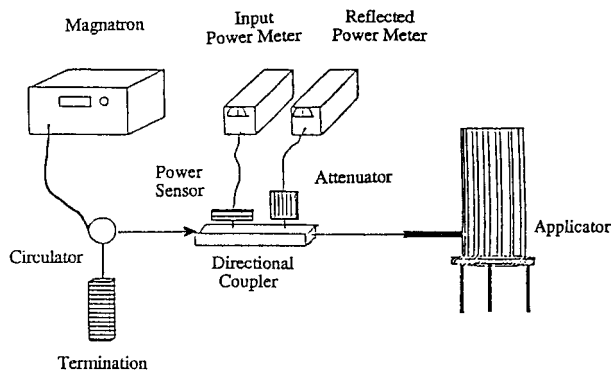


Figure 1 Schematic illustration of the instrumentation utilized for microwave processing.

stirring and the reaction was further degassed. The hot resin was subsequently poured into hollow cylindrical Teflon molds. The melts were cured in a cylindrical microwave cavity, at a frequency of 2.45 GHz. The temperature of the sample was continuously monitored during the course of the reaction via a Luxtron (Model 750) fiber optic temperature probe. The desired temperatures were maintained to ± 3 – 5°C by either varying the source power or by intermittently tuning and detuning the cavity, thereby varying the reflected power. It is assumed that influences on the heating rate due to heats of reaction are negligible. A schematic of the instrumentation utilized for microwave curing is represented in Figure 1. Details of the instrumentation involved are available elsewhere.^{1–3,5} Several defined modes exist within the cylindrical microwave cavity. The TE_{111} mode was employed to process the polymers. This mode was generated by adjusting the height of the cavity with a sliding short. The cylindrical cavity is very effective as the radiation from the generator is continuously reflected from the walls, thus passing through the specimen many times until it is absorbed. Coaxial directional couplers, attenuators, and power meters which measure the input power, reflected power, and transmitted power are attached between the generator and the cylindrical applicator. The power meters and the temperature-measuring system are attached to an IBM PC for data collection. The power meters allow the cavity to be tuned or detuned for temperature control.

Three sets of different experiments were carried out with the 15K PPH–PSF–OH reactive modifier. The first set consisted of 25 wt % of thermoplastic-modified cyanate ester resin samples that were cured in the microwave employing three

different cure cycles. The second set consisted of subjecting cyanate ester resin melts with different weight percent composition of the 15K PPH–PSF–OH modifier to the same microwave cure protocol and studying the resulting morphologies. The third set of experiments involved a study on samples of resin melt consisting of 25 wt % 15K PPH–PSF–OH thermoplastic being subjected to varying initial input powers. The morphologies in all these materials were studied by scanning transmission electron microscopy (STEM). Analyses were performed on microtomed thin sections of samples stained with ruthenium oxide. Ruthenium oxide exhibits a preferential staining of the thermoplastic phase, thereby serving as an effective tool in analysis of the morphologies. Analyses were performed on a Phillips 420T electron microscope utilizing a back-scattered detector.

RESULTS AND DISCUSSION

The characterization results on the hydroxyl [PPH–PSF–OH] and *t*-butyl phenyl [PPH–PSF–*t*Bu]-functionalized phenolphthalein-based amorphous poly(arylene ether sulfone) oligomers are given in Table I. Based on our earlier studies,^{14,15} it was expected that the hydroxy-functionalized oligomers would serve as a potentially reactive modifier whereas the *t*-butylphenyl-functionalized oligomers would serve as a nonreactive control.

Initially, feasibility studies were conducted to ascertain the optimum conditions for microwave processing (curing) of the unmodified cyanate ester resin. The heating rate was fast in the beginning as the molten system ($\text{mp} = 79^\circ\text{C}$) was placed in the cavity. The heating rate became slower as the system temperature approached 160°C . At this point, the rate of chemical reactions and the consequent exothermic heat resulted in a tremendous acceleration of the heating rate. Autoacceleration resulted subsequently and the sharp temperature rise was very hard to control by either detuning the cavity or by lowering the input power. Such an uncontrolled process resulted in a charred product. In certain cases when the product was not charred (by effectively switching off the microwave radiation during the initial course of autoacceleration), the reactions were determined to be incomplete, thus resulting in a partially cured product. However, it was difficult to reheat this material as extensive cross-linking had already taken place. As a result of the

Table I Solution and Thermal Characterization of Hydroxy and *t*-Butyl Phenyl-Functionalized Phenolphthalein-based Poly(arylene ether sulfone) Oligomers

Polymer Type	Theoretical $\langle M_n \rangle$	$[\eta]$ CHCl ₃ , 25°C (dL/g)	$\langle M_n \rangle$	T_g °C DSC, 10°C/min
PPH-PSF-tBu	15,000	0.25	16,000 ^a	258
PPH-PSF-OH	15,000	0.26	15,500 ^b	259

^a Titration of phenolic end groups with 0.025*N* TMAH.

^b ¹H-NMR: Ratioing methyl protons of *t*-butylphenyl end group to main chain aromatic protons.

crosslinking, the material was transformed into a glassy state and the lower mobility of the polymer segments resulted in a lower dielectric loss and, consequently, a very slow heating rate. This is evident from Figure 2 wherein the dielectric loss at 1 kHz is plotted as a function of temperature, for a fully cured cyanate ester network. The cured material exhibits two low-temperature secondary relaxations at -70 and 70°C, respectively. However, the magnitude of these loss peaks is so small that it is insufficient to achieve sufficient dipolar heating of the material using microwave radiation at low temperatures. The dielectric loss peak arising due to the glass transition process begins at

250°C. Once again, the low intensity of this peak accounts for the low heatability of the cured network by microwave radiation.

In the case of the thermoplastic-modified systems, the presence of the thermoplastic modifier provided two specific advantages: First, the presence of the dipoles on the thermoplastic backbone led to vastly improved control over the system temperature and the heating rates. It was seen that the system temperature and the heating rates were effectively controlled by either varying the input power or by detuning the cavity. Second, the presence of the polar thermoplastic material also ensured that the material could be main-

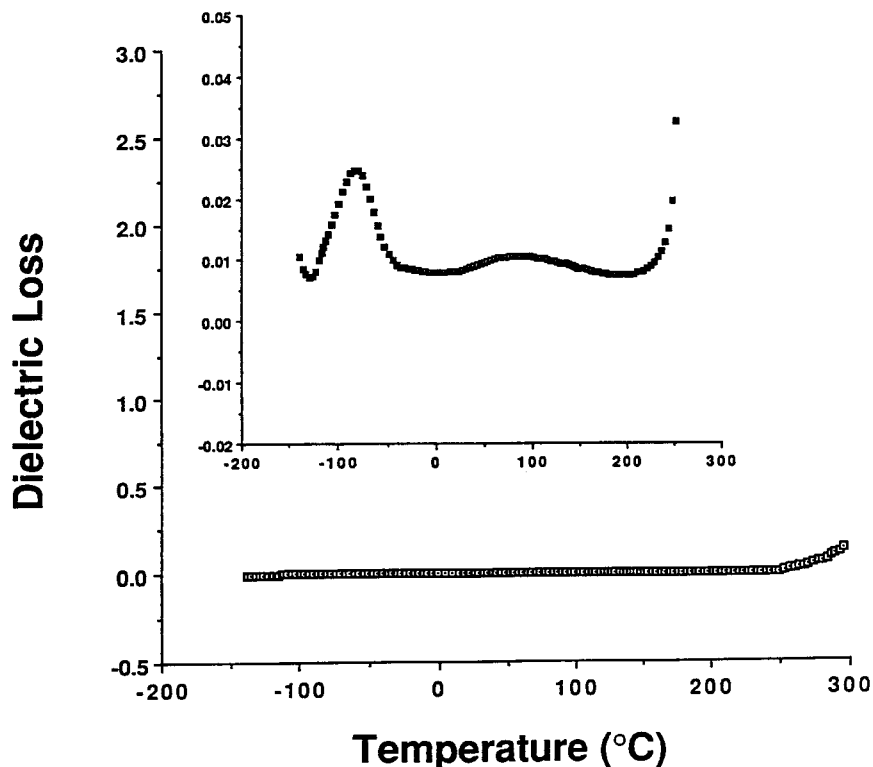


Figure 2 Dielectric spectra showing dielectric loss vs. temperature (°C) at 1 kHz for the fully cured cyanate ester network. (Insert: expanded spectrum.)

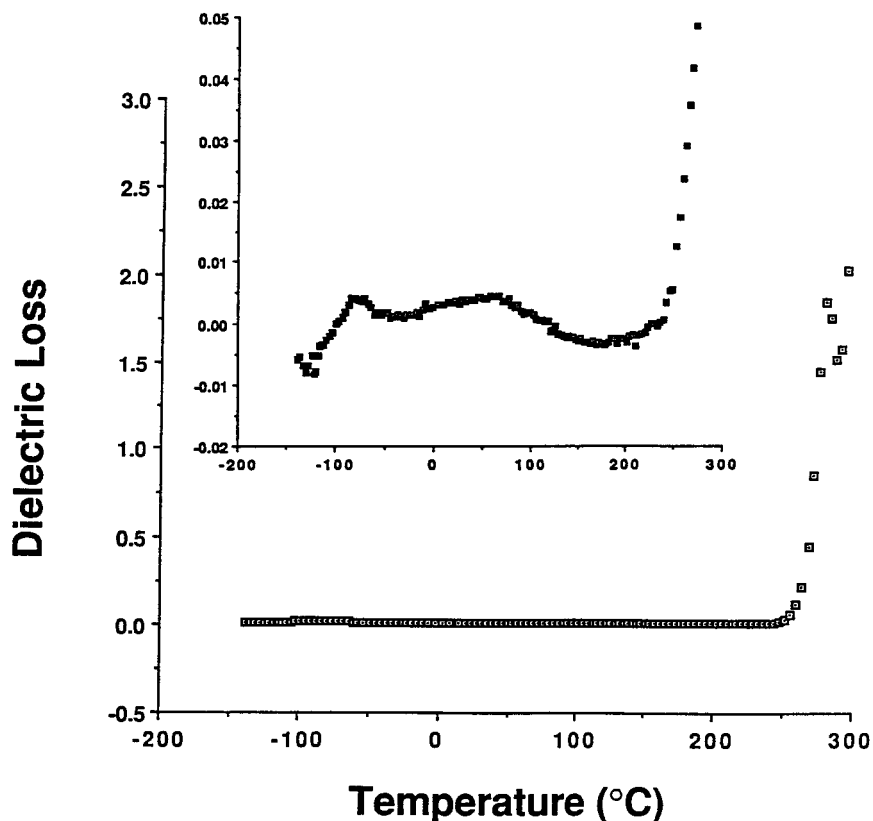


Figure 3 Dielectric spectra showing dielectric loss vs. temperature ($^{\circ}\text{C}$) at 1 kHz for the 15K PPH-PSF-OH thermoplastic modifier. (Insert: expanded spectrum.)

tained at elevated temperatures, even after significant extents of the reaction had taken place, thereby enabling the material to be fully cured. This is further explained on the basis of the dielectric loss vs. temperature profile (Fig. 3) obtained at 1 kHz on the 15K PPH-PSF-OH thermoplastic material. The thermoplastic exhibits two low-temperature secondary relaxations at -85°C and at about 90°C , respectively. However, the magnitude of these loss peaks is so small that it is insufficient to achieve sufficient dipolar heating of the material using microwave radiation at low temperatures. A comparison of Figures 2 and 3 suggests that the dielectric loss peak due to the glass transition is significantly higher in the case of the thermoplastic relative to the unmodified cured cyanate ester network. In addition, the onset of the peak due to the glass transition process occurs at a much lower temperature in the case of the thermoplastic. Thus, the presence of the thermoplastic modifier in the cyanate ester network serves to heat the material as well as to maintain a stable viscosity of the material at elevated temperatures.

Effect of Varying Cure Cycle

Figure 4 represents STEM images of microtomed RuO_4 -stained thin sections of 25 wt % 15K PPH-PSF-OH-modified cyanate ester networks cross-linked employing microwave radiation. A typical profile of the input power and reaction temperature as a function of time is represented in Figure 5. The initial input power, unless otherwise stated, was always held at 6 W. (As will be seen later in this section, the initial input power is an additional variable that influences the final cured-state morphology.) This profile has been approximated as a "180 s/ 200°C , 800 s/ 250°C " cure cycle in Figure 4. The extent of reaction in all the three cases (Fig. 4) was estimated by DSC to be 97–98%. In contrast to the long thermal cure cycles (Fig. 6 of Ref. 11), the networks via microwave cure (Fig. 4) had been generated in a few minutes. It is seen that in the case of the microwave-cured 25 wt % 15K PPH-PSF-OH-modified cyanate ester networks a faster cure (800 s/ 250°C) results in a relatively finer morphology in comparison to the morphologies obtained with slower cure cycles

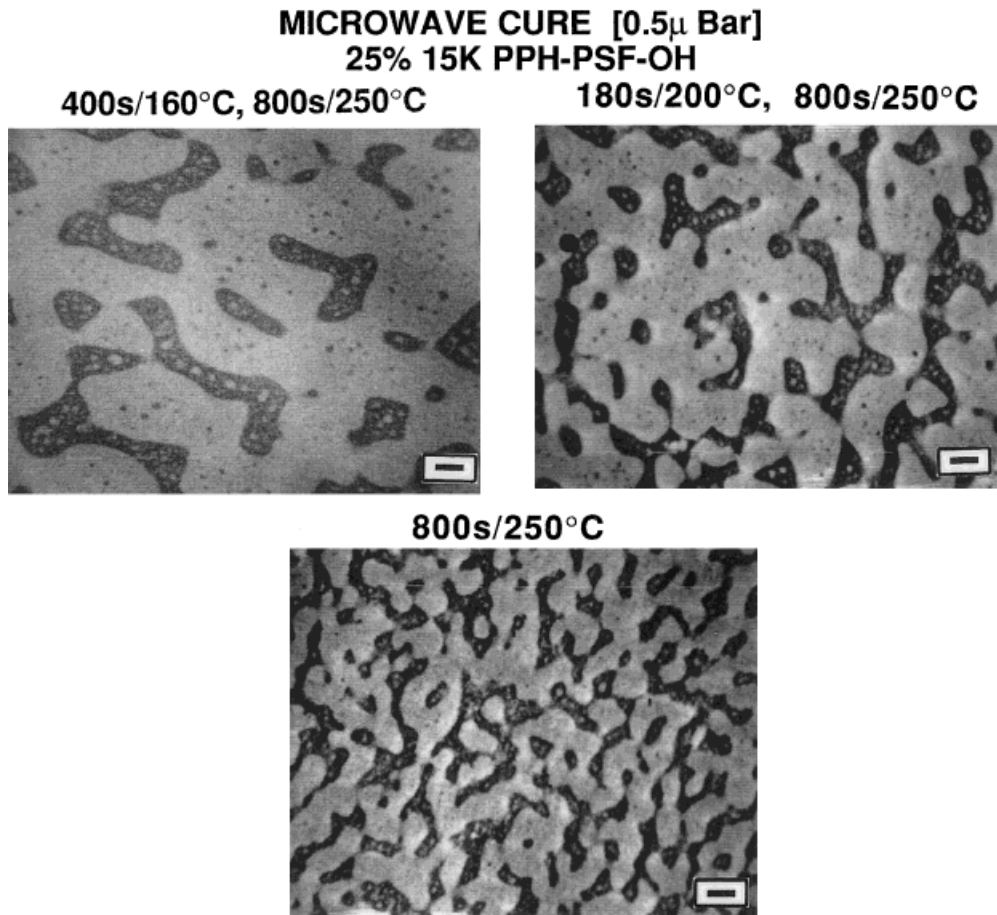


Figure 4 STEM image of RuO₄-stained thin sections of 25 wt % 15K PPH-PSF-OH-modified networks. [Bar = 0.5 μ .] Microwave cure: effect of varying cure cycle.

of “400 s/160°C, 800 s/250°C” or “180 s/200°C, 800 s/250°C.” Thus, a comparison of the morphological developments during thermal (Fig. 6 of

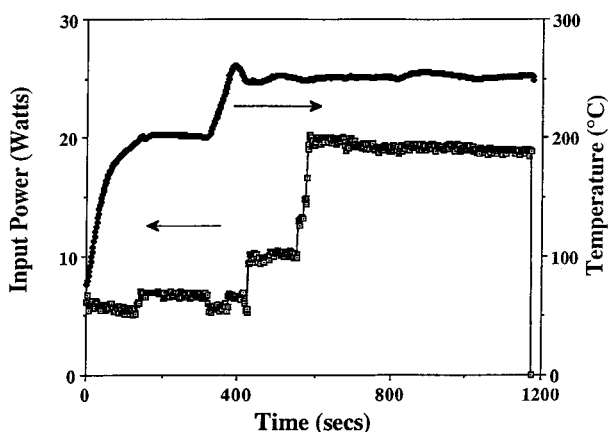


Figure 5 Typical profile of input power (W) and reaction temperature (°C) as a function of time (s) during microwave cure.

Ref. 11) and microwave cure (Fig. 4) appears to suggest two contrasting trends. In the case of the thermally cured networks, a slower cure results in finer morphologies relative to the faster-cured networks. However, in the case of the microwave-cured networks, a faster cure results in finer morphologies relative to the slower-cured networks. Further experimentation is required for a possible explanation regarding this aspect.

Shown in Figure 6 are STEM micrographs of ruthenium oxide-stained microtomed thin sections of 15K PPH-PSF-tBu-modified cyanate ester networks. The stained regions correspond to the presence of the phenolphthalein-based poly(arylene ether sulfone) phase. The thermoplastic concentration was kept constant at 25 wt %. In contrast to the well-defined morphologies of 15K PPH-PSF-OH-modified networks (Fig. 4), the 15K PPH-PSF-tBu-modified networks exhibited gross macrophase separation with no apparent control over the sizes of the phase-separated domains.

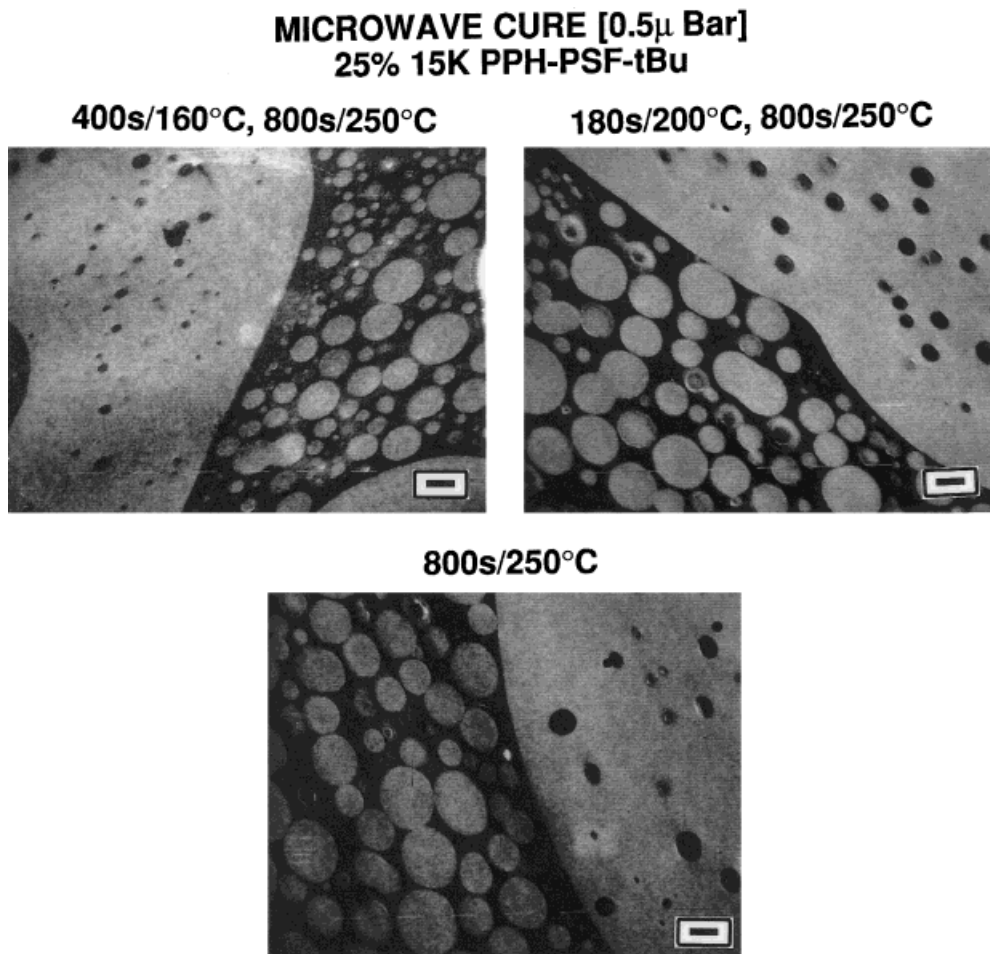


Figure 6 STEM image of RuO₄-stained thin sections of 25 wt % 15K PPH-PSF-tBu-modified networks. [Bar = 0.5 μ .] Microwave cure: effect of varying cure cycle.

Influence of Reactive Thermoplastic Modifier ($\langle M_n \rangle = 15,000$)

Figure 7 represents STEM images of microtomed RuO₄-stained thin sections of networks with varying compositions of 15K PPH-PSF-OH, crosslinked employing microwave radiation. The dark-stained regions correspond to the presence of ruthenium oxide-stained thermoplastic domains. At 10 and 20 wt % loadings of 15K PPH-PSF-OH, the morphology is essentially a continuous phase of the cyanate ester network with a dispersed phase of the thermoplastic. Thirty weight percent loadings of the thermoplastic results in nearly a phase-inverted morphology, wherein the thermoplastic appears to be the continuous phase. A comparison of the morphologies generated via thermal (Fig. 8 of Ref. 12) and microwave cures (Fig. 7) suggests that the microwave-cured networks exhibit much larger phase sizes relative to the thermally cured networks. However, such a

generalization is not necessarily true, as it has been demonstrated that morphology is a variable and varies with, among other factors, the rates and mechanism of cure.

At a 20 wt % concentration of 15K PPH-PSF-OH, the morphology in the case of the thermal cure was one of the cocontinuous type (Figs. 1, 2, and 6 of Ref. 11). However, in the case of the microwave-cured networks (Fig. 7), at a 20 wt % concentration of 15K PPH-PSF-OH, the morphology is essentially a continuous phase of the cyanate ester network with a dispersed phase of the thermoplastic. A comparison of the morphologies generated via thermal and microwave cures suggests that the point of phase inversion occurs at a higher thermoplastic concentration in the case of the microwave-cured networks. However, once again, such a generalization is not necessarily true, as it has been demonstrated that morphology is a variable.

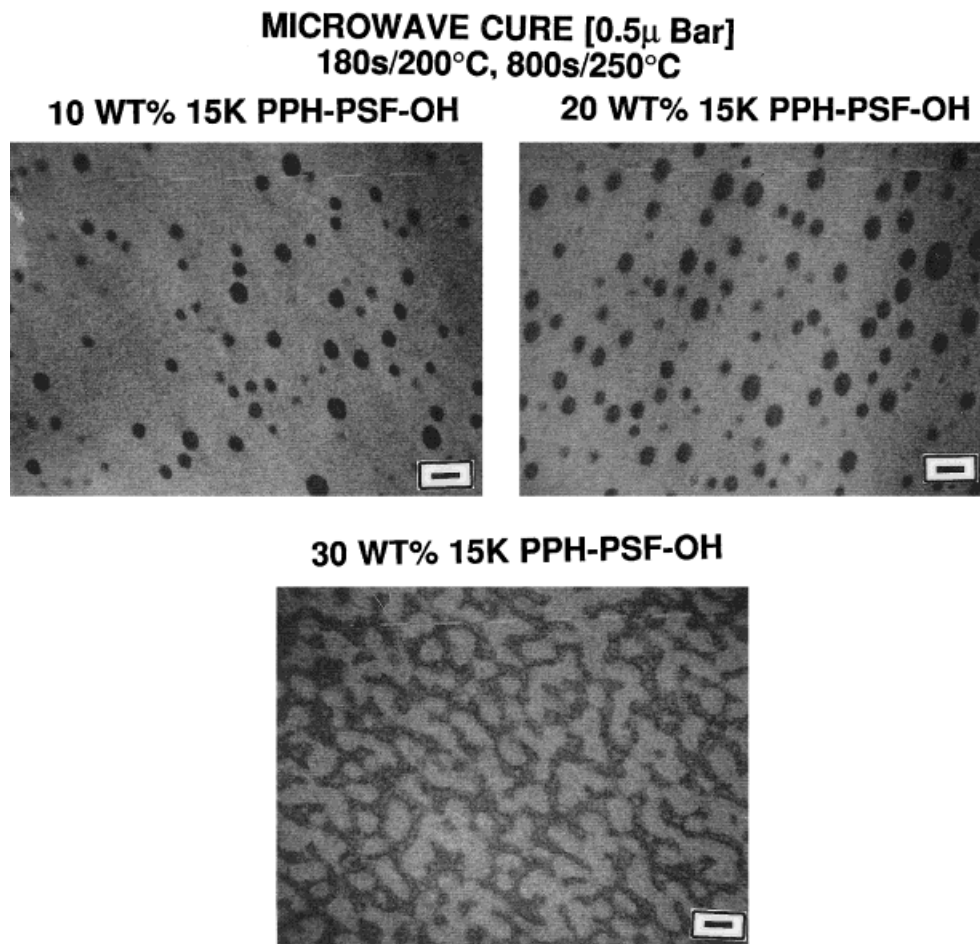


Figure 7 STEM images of RuO₄-stained thin sections of networks with varying compositions of 15K PPH-PSF-OH. [Bar = 0.5 μ .] Microwave cure: effect of varying modifier concentration.

Effect of Varying the Initial Input Power

In the case of the microwave-cured networks, the initial input power is an additional variable that influences the final cured-state morphology. Seen in Figure 8 are STEM images of microtomed RuO₄-stained thin sections of networks with varying levels of input power from 10 to 25 W. The thermoplastic concentration was held constant at 25 wt % in all cases. The corresponding profiles were approximated as “180 s/200°C, 800 s/250°C.” It is seen from Figure 8 that the initial input power does influence the morphology. The influence is more pronounced in the case of networks cured using an initial input power of 25 W, in that the morphology is relatively finer in comparison to the networks cured with an initial input power of 10–20 W. This once again suggests that in the case of the microwave-cured networks a faster cure results in finer morphologies relative

to the slower-cured networks. Such an observation is in agreement with the observations in Figure 4.

CONCLUSIONS

Controlled molecular weight phenolphthalein-based poly(arylene ether sulfone)s which were quantitatively functionalized with either hydroxyl or *t*-butylphenyl end groups were synthesized and characterized. The functionalized oligomers were subsequently cocured with commercially available bisphenol-A-based cyanate ester resins to generate thermoplastic-modified networks.

Attempts to process the unmodified cyanate ester resin employing microwave radiation resulted in either a charred or an incompletely cured prod-

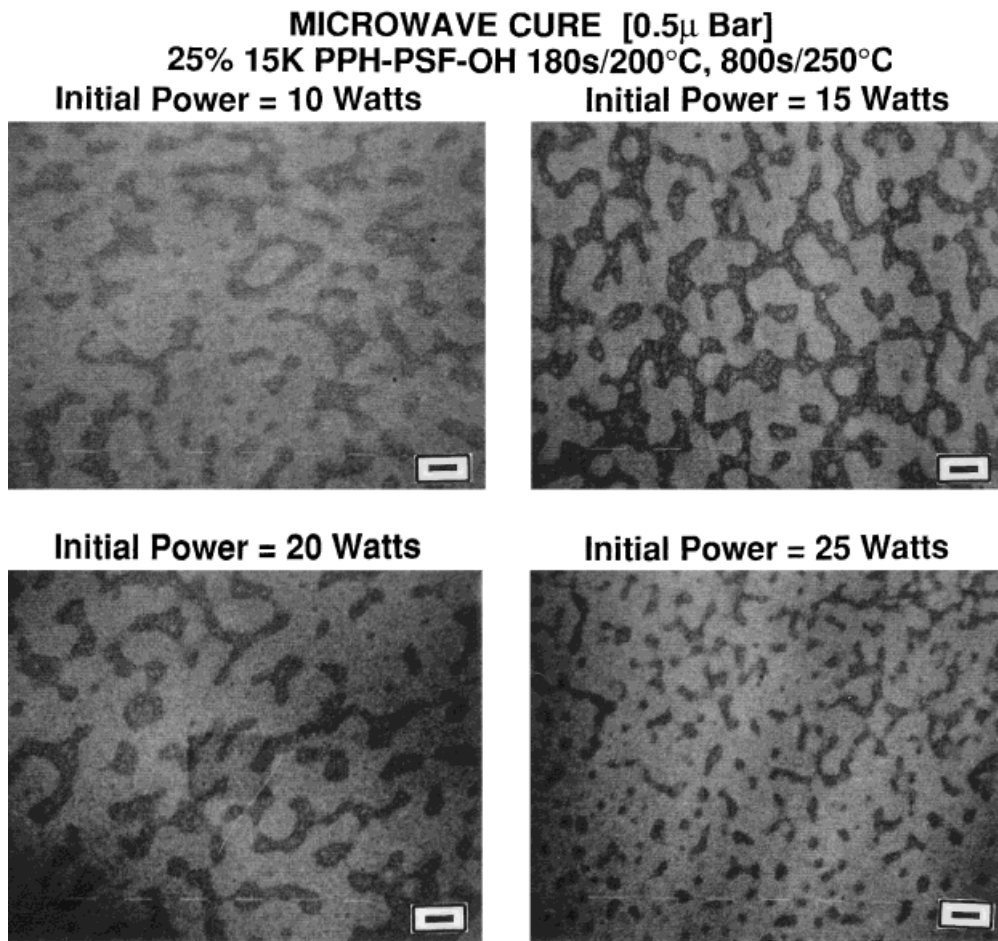


Figure 8 STEM image of RuO₄-stained thin sections of 25 wt % 15K PPH-PSF-OH-modified networks. [Bar = 0.5 μ .] Microwave cure: effect of varying initial input power.

uct. Charred products were obtained as a result of the exothermic reaction and the consequent tremendous acceleration of the reaction rate. In certain cases when the autoacceleration was contained, an incompletely cured product was obtained. It was not possible to further cure the incompletely cured materials. This was attributed to the low dielectric loss of the material. In the case of the thermoplastic-modified networks, the addition of the thermoplastic led to vastly improved control over the system temperature and the heating rates and also ensured that the material could be maintained at elevated temperatures, thereby enabling the material to be fully cured. It was possible to process the thermoplastic-modified resin materials to very high conversions (97–98%) within minutes.

In the case of the 25 wt % 15K PPH-PSF-OH-modified networks, it was possible to vary the morphology by either varying the cure cycle em-

ploying constant initial input power or alternatively by varying the levels of initial input power. In both cases, networks generated with a faster cure exhibited much finer morphologies relative to the morphologies in networks that were cured more slowly. It has been demonstrated that in contrast to the well-defined morphologies of the reactive thermoplastic-modified networks the use of nonreactive modifiers of the same molecular weight and backbone chemistry results in gross macrophase separation with no apparent control over the sizes of the phase-separated domains.

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