

Amorphous Phenolphthalein-Based Poly(arylene ether)-Modified Cyanate Ester Networks: Effect of Thermal Cure Cycle on Morphology and Toughenability

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ABSTRACT: Reactive functional thermoplastic poly(arylene ether) toughness modifiers were demonstrated to enhance toughness of brittle thermosetting cyanate ester networks and also allowed retention of a highly desirable stability to solvent stress cracking and a moderately high modulus. Careful control of the heterophase morphological structure was necessary to achieve significant toughening. In contrast to the well-defined morphologies of the reactive thermoplastic-modified networks, the use of nonreactive simple physical blend modifiers of the same molecular weight and backbone chemistry produced a macrophase separation and no apparent control over the sizes of the phase-separated domains. Macrophase-separated morphologies are inherently process-sensitive and less desirable from the point of performance control and prediction. Generation of controlled microphase-separated morphologies can be achieved by systematically varying thermal cure cycles in the case of the reactive thermoplastic-modified systems. Such a cure cycle dependence of the morphology was particularly demonstrated for the case of the 25 wt % 15,000 (M_n) (15K) phenolphthalein-based hydroxy-functionalized poly(arylene ether sulfone) (PPH-PSF-OH)-modified networks. Morphologies that exhibit finer textures of the phase separated domains usually result in lower fracture toughness values. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 167–178, 1997

INTRODUCTION

Cyanate ester networks are receiving considerable attention as low dielectric, low moisture absorption candidates for high-temperature adhesives and composite applications such as in printed circuit boards.^{1–3} Low toughness is a major drawback with most crosslinked thermosetting materials, including the cyanate ester networks. Attempts have been made at improving the toughness of cyanate ester networks and their

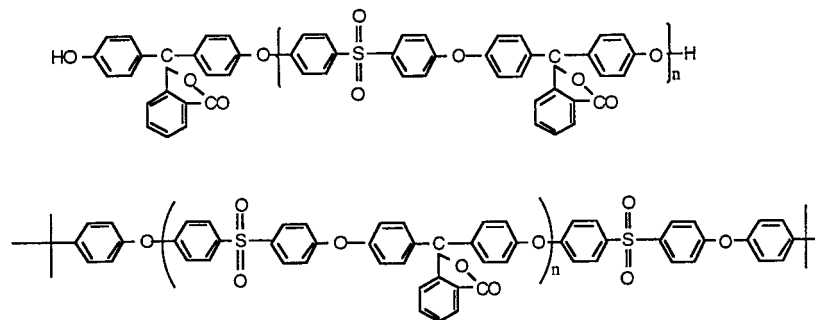
fiber-reinforced composites (based on cyanate ester as the matrix resin). These include modifications with siloxanes,⁴ other rubbers,⁵ and engineering thermoplastics.^{6–8} Considerable attention has been devoted to the aspect of toughening such brittle networks in our laboratories, which has sought 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, molecular weight, and end-group functionality. We have investigated and reported the use of controlled molecular weight-functionalized amorphous bisphenol-A-based polysulfones ($T_g \sim 175^\circ\text{C}$) and poly(ether ketones) ($T_g \sim 155^\circ\text{C}$) as potential toughness modifiers.⁹ Careful control of the heterophase morphological structure is necessary to achieve significant

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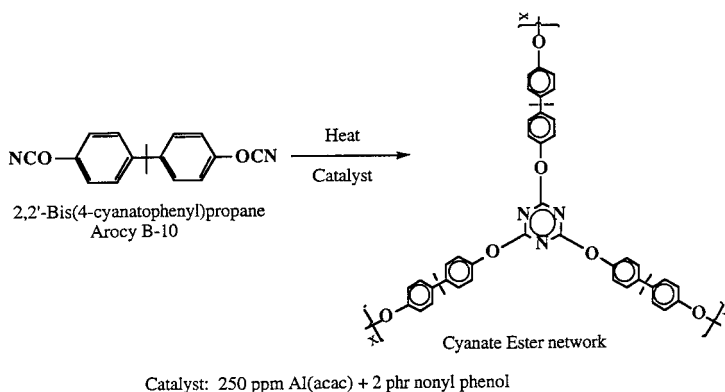
Scheme 3 Hydroxy (PPH-PSF-OH)- and *t*-butylphenyl (PPH-PSF-*t*Bu)-functionalized phenolphthalein-based poly(arylene ether)s employed in this study.

scanned at 10°C/min to $T > T_g$, quenched to room temperature, and rescanned at 10°C/min. The T_g values reported are those from second scans.

Preparation and Characterization of Hot-melt Blends of Cyanate Ester Resin with Thermoplastic Modifiers

The amorphous polymers were dissolved in a molten AroCy B-10 cyanate precursor 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 ppm Al(acac)/2 phr nonyl phenol] was added with stirring and the reaction was further degassed. The hot resin was subsequently poured into preheated (100°C) silicone rubber molds for fracture toughness (K_{1C}) and tensile dog-bone and 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” and subsequently cooled at 1–2°C/min unless otherwise specified. The postulated chemical processes leading to three-dimensional insoluble networks are represented in Scheme 4.^{3,24–26}

Infrared spectroscopy measurements were performed on a Nicolet-800 FTIR spectrophotometer employing thin films of the resin coated onto a NaCl salt plate. Dynamic mechanical analysis (DMA) analyses were performed on a Perkin-Elmer DMA-7 analyzer in the three-point bending mode. Tests were conducted at a frequency of 1 Hz employing a dynamic temperature scan rate of 3°C/min. Dynamic mechanical thermal analysis (DMTA) analyses were performed on a Polymer Laboratories DMTA analyzer in the bending mode. Tests were conducted at multiple frequencies employing a dynamic temperature scan rate. Fracture toughness (K_{1C}) measurements were conducted in accordance with the ASTM D-5045-91 (E-399-90) test method on 10–12 specimens of dimensions 3.2 × 6.5 × 38 mm. The samples were notched at the center to a depth of approximately 0.5 mm using a reciprocating saw. Sharp cracks were then initiated (with a fresh surface of a razor blade) by employing a 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



Scheme 4 Cyclotrimerization of cyanate esters.

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

Polymer Type	Theoretical $\langle M_n \rangle$	$[\eta]^a$ (dL/g)	$\langle M_n \rangle^b$ Titration	T_g °C ^c
PPH-PSF- <i>t</i> Bu	15K	0.25	16,000 ^d	258
PPH-PSF-OH	15K	0.26	15,500	259

^a In CHCl₃ at 25°C.^b Titrated with 0.025N TMAH.^c DSC 10°C/min.^d ¹H-NMR.

loaded onto a three-point bend fixture attached to an Instron and tested at a rate of 0.05 in./min. Scanning transmission electron microscopy (STEM) analysis were performed on microtomed thin sections of samples stained with ruthenium oxide. 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*-butylphenyl (PPH-

PSF-*t*Bu)-functionalized phenolphthalein-based amorphous poly(arylene ether sulfone) oligomers, are given in Table I, the latter producing a simple physical blend. Based on our earlier studies,⁹ 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.

All comparisons with respect to properties like tensile properties, fracture toughness, etc., in this study were made relative to the unmodified fully cured network. Values for simple blends were published earlier.⁹ This required that any cure

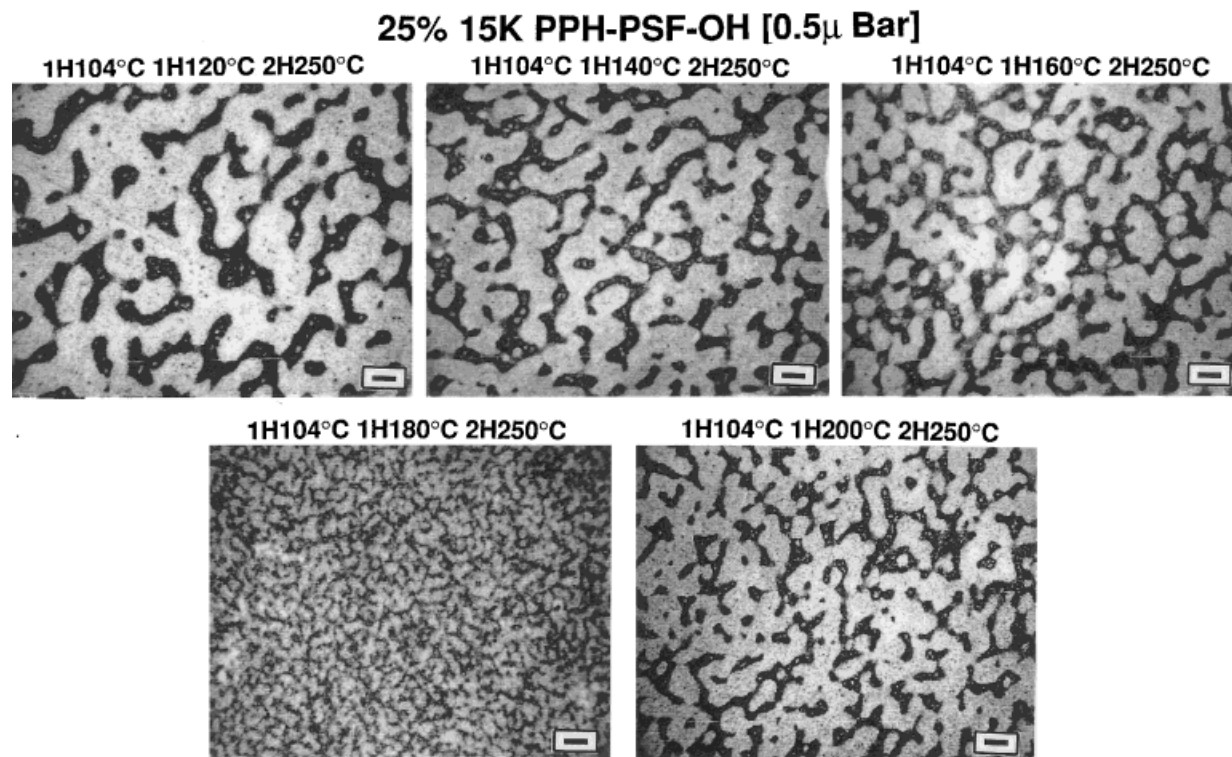
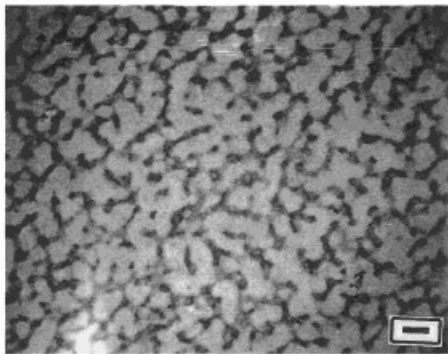


Figure 1 STEM of 25 wt % 15K PPH-PSF-OH-modified networks: effect of cure cycle on morphology. (Bar = 0.5 μ.)

25% 15K PPH-PSF-OH [0.5 μ Bar] 3H104°C 1H200°C 2H250°C



1H104°C 1H200°C 2H250°C

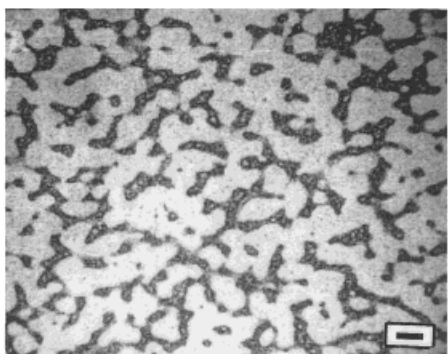


Figure 2 STEM of 25 wt % 15K PPH-PSF-OH-modified networks: effect of cure cycle on morphology. (Bar = 0.5 μ .)

cycle employed in this study should result in a fully cured network. The cure cycle most commonly employed in this study was “3 h/104°C, 1 h/200°C, 2 h/250°C,” with a ramp rate of 4–5°C/min between steps. Throughout this study, the catalyst/cocatalyst concentration was kept constant at 250 ppm Al(acac) in 2 pph nonyl phenol. The extent of the reaction attained with such a cure cycle was estimated by FTIR and gel fraction experiments to be > 99%. The decrease in peak height due to the 2270 cm^{-1} C \equiv 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 employed, the final stage always involved a “2 h/250°C” cure. This ensured that the networks in all cases were fully cured. The unmodified cured networks had a T_g of 265–270°C as detected by DMA at a frequency of 1 Hz.

Comparison of Morphologies with Reactive and Nonreactive Modifiers

In Figures 1 and 2 are presented STEM micrographs of ruthenium oxide-stained microtomed

thin sections of 25 wt % 15K PPH-PSF-OH-modified cyanate ester networks. The stained regions correspond to the presence of the phenolphthalein-based poly(arylene ether sulfone) phase. The final stage involved a “250°C cure for 2 h” in all cases, thereby ensuring that the networks were fully cured and were of comparable glass transition temperatures. Shown in Figure 3, are STEM micrographs of ruthenium oxide-stained microtomed thin sections of 25 wt % 15K PPH-PSF-*t*Bu-modified cyanate ester networks. Once again, the stained regions correspond to the presence of the phenolphthalein-based poly(arylene ether sulfone) phase. In contrast to the well-defined morphologies of 15K PPH-PSF-OH-modified networks (Figs. 1 and 2), the 15K PPH-PSF-*t*Bu-modified networks exhibited gross macrophase separation with no apparent control over the sizes of the phase-separated domains. This aspect serves to further reinforce the apparent reaction of the hydroxyl end groups into the cyanate ester network. In our earlier work,⁹ we demonstrated that either hydroxyl or cyanato end groups effectively react into the cyanate ester network and thereby afford networks with improved toughness and stability to solvent stress cracking. Such improvements were attributed to the formation of a chemical link between the thermoplastic modifiers and the thermosetting phase, thus resulting in a strong interface. The hydroxyl- or cyanato-functionalized modifiers were much superior to the nonreactive *t*-butyl-functionalized modifiers, in terms of both mechanical performance and solvent stability. The gross macrophase-separated morphologies as in Figure 3 would likely result in no control whatsoever over the interface and likely the mechanical performance. In addition, from the point of view of performance control and prediction, controlled microphase-separated morphologies are desirable.

Effect of Cure Cycle on Morphology

In Figure 1 are presented STEM micrographs of ruthenium oxide-stained microtomed thin sections of 25 wt % 15K PPH-PSF-OH-modified cyanate ester networks. The different cure cycles that were employed are as represented in Figure 1. In all cases, the cure cycles involved an initial hold for 1 h/104°C and a final postcure for 2 h/250°C. The ramp rates between steps was 4–5°C/min. The final stage involved a 250°C cure for 2 h in all cases, thereby ensuring that the networks were fully cured and were of comparable glass

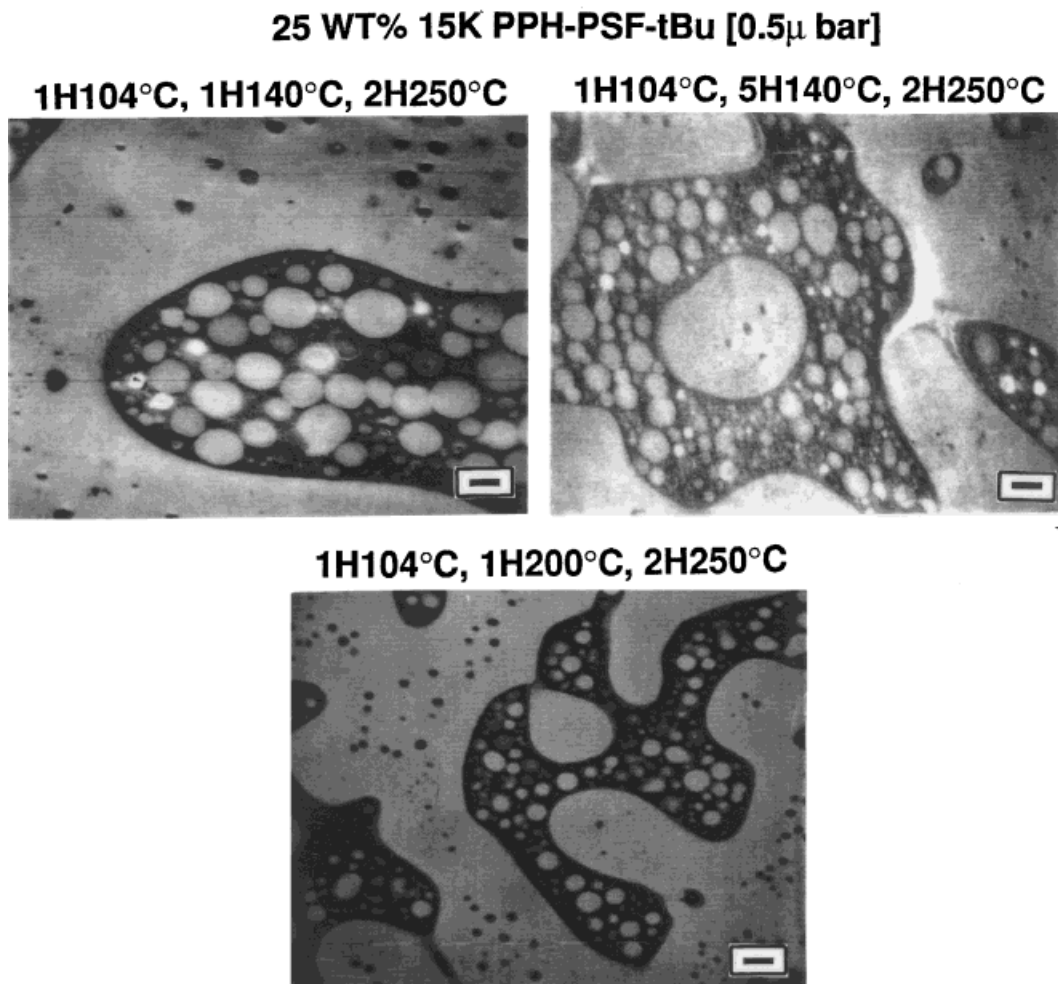


Figure 3 STEM of 25 wt % 15K PPH-PSF-tBu/simple blend-modified networks: effect of cure cycle on morphology. (Bar = 0.5 μ .)

transition temperatures. The resulting morphologies (Fig. 1) suggest the possible dependence of morphologies on the cure cycle employed. The extent of reaction following a 3 h/104°C cure is negligible and is less than 1%, as verified by DSC and FTIR analysis. In addition, it is seen from Figure 2 that the use of either a “1 h/104°C, 1 h/200°C, 2 h/250°C” or a “3 h/104°C, 1 h/200°C, 2 h/250°C” cure cycle results in fairly similar morphologies. The dependence of fracture toughness on the morphologies (Fig. 1) of the corresponding networks is seen in Figure 4. It is seen from Figures 1 and 4 that in the case of the 25 wt % 15K PPH-PSF-OH-modified networks morphologies that exhibited finer textures with respect to the sizes of the phase-separated domains translated into lower fracture toughness values.

STEM micrographs of ruthenium oxide-stained microtomed thin sections of networks modified

with 10 wt % of 15K hydroxy-functionalized phenolphthalein-based poly(arylene ether sulfone) are shown in Figure 5. The different cure cycles that were employed are as represented in Figure 5. Once again, all cure cycles involved an initial hold for 1 h/104°C and a final postcure for 2 h/250°C. It is seen from Figure 5 that in the case of the 10 wt % 15K PPH-PSF-OH-modified networks changes in morphology with changing cure cycles are not as marked as was the case with the 25 wt % 15K PPH-PSF-OH-modified (Fig. 1) networks. The fracture toughness values (Fig. 4) of the 10 wt %-modified networks were very similar in all cases.

The dependence of the morphology on the cure cycle is further illustrated in Figure 6 for the case of the 15K PPH-PSF-OH-modified networks. Once again, all samples in Figure 6 were of the same composition, i.e., 25 wt % thermoplastic. The

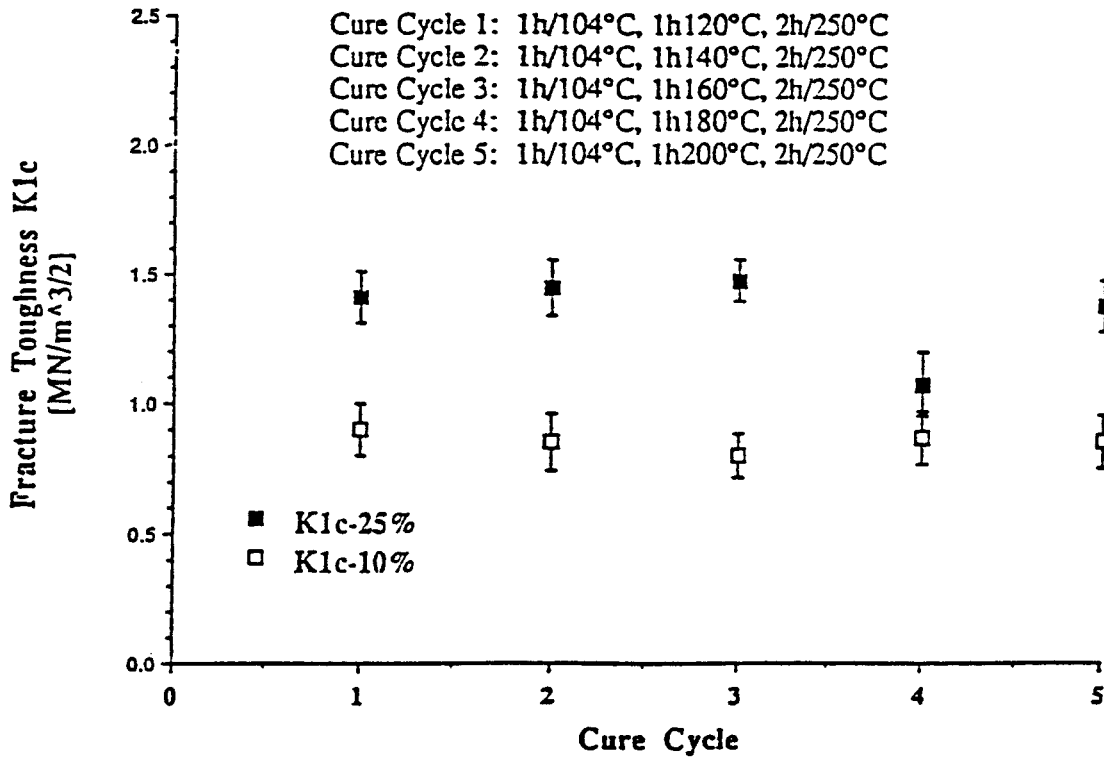


Figure 4 Fracture toughness (K_{1C}) as a function of cure cycle of the 15K PPH-PSF-OH modified networks.

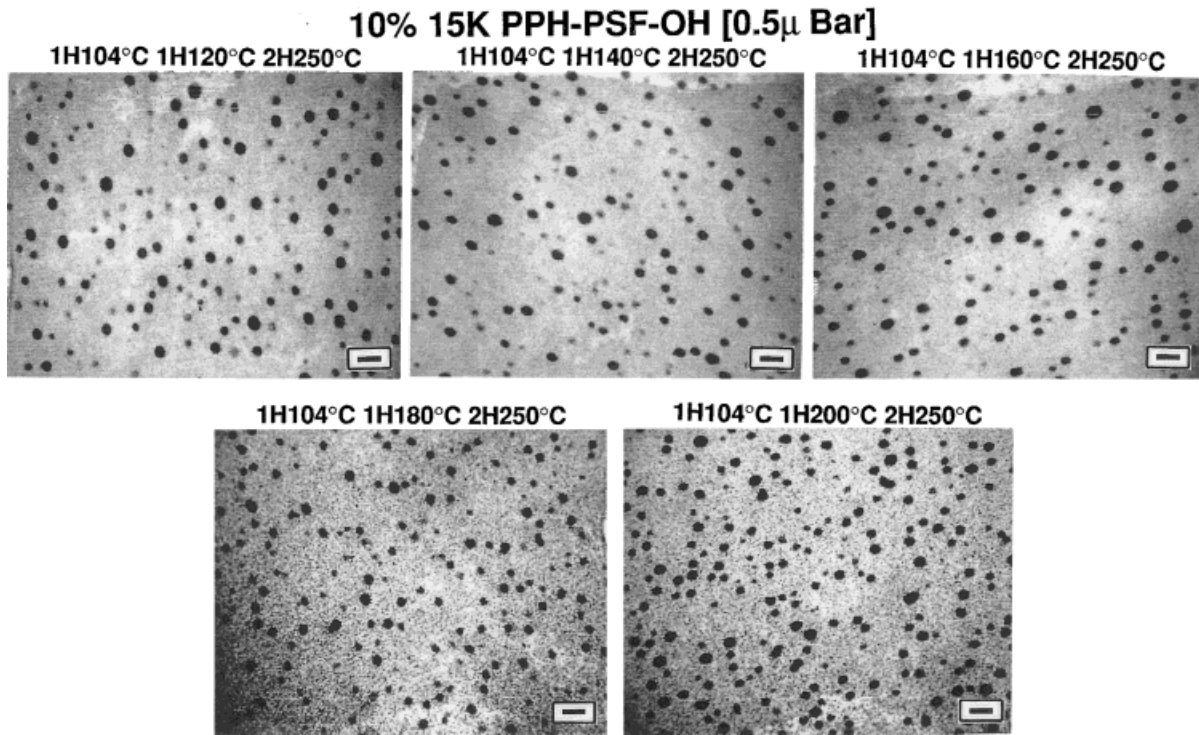


Figure 5 STEM of 10 wt % 15K PPH-PSF-OH-modified networks: effect of cure cycle on morphology. (Bar = 0.5 μ .)

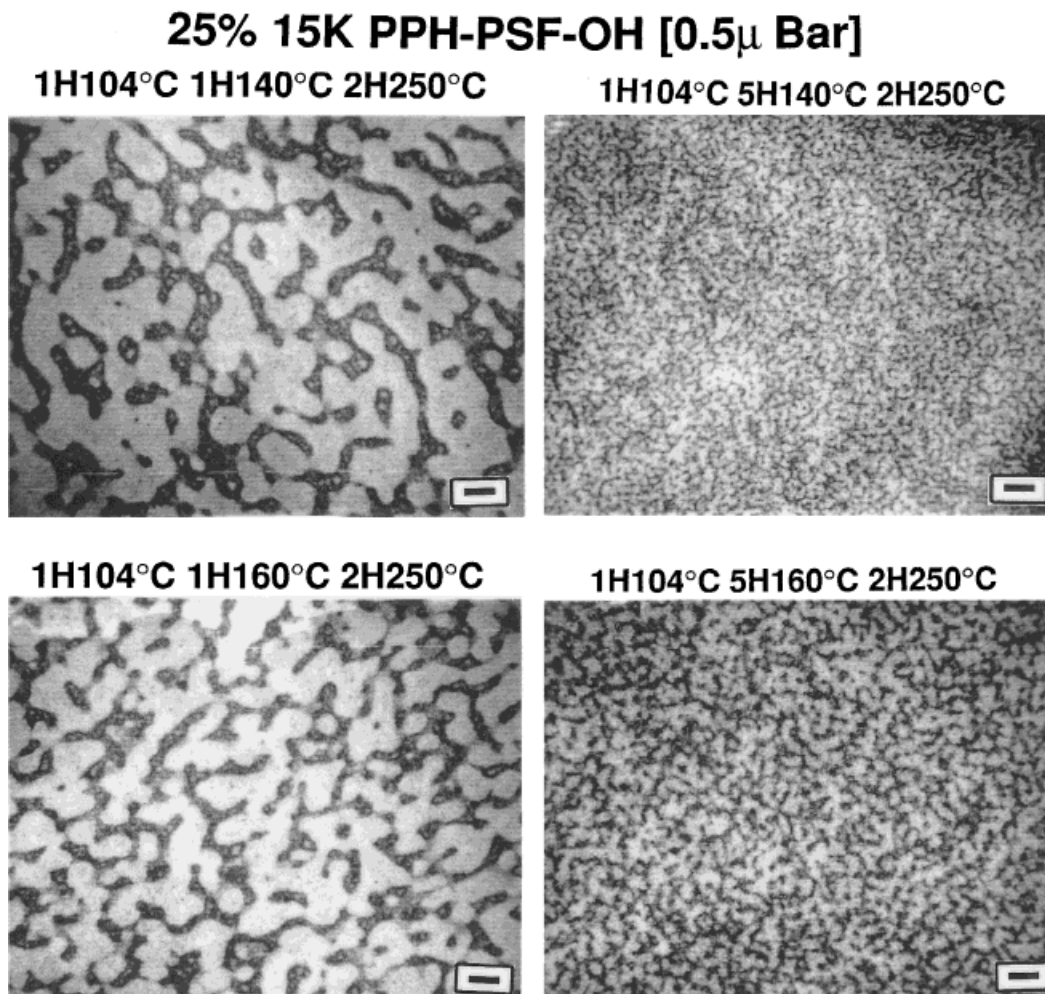


Figure 6 STEM of 25 wt % 15K PPH-PSF-OH-modified networks: effect of cure cycle on morphology. (Bar = 0.5 μ .)

final stage “250°C cure for 2 h” in all cases ensured that the networks were fully cured and were of comparable glass transition temperatures. It is seen from Figure 6 that samples that were cured more slowly (slower rate of conversion) developed finer textures relative to those that were cured faster. For example, the sizes of the phase-separated domains were much larger in the case of networks formed by employing a “1 h/104°C, 1 h / 160°C, 2 h/250°C” cure cycle relative to those that were formed by employing a “1 h/104°C, 5 h / 160°C, 2 h/250°C” cure cycle. It is reasonable to expect that varying morphologies as in Figure 6 would exhibit contrasting mechanical properties.

The formation of finer textures could be attributed to either “enhanced phase mixing” or to “the gradual decrease of ‘dispersed phase sizes’ owing to the decreasing ‘mesh size’ of the network.”

DMTA analyses (Fig. 7) of these networks did not show up much of a distinguishable difference in terms of the extents of phase mixing, possibly due to the close proximities of the glass transition temperatures of the thermoplastic and thermosetting components. Figure 8 represents attempts to follow the morphological developments during cure in the specific case of networks cured employing either a “1 h/104°C, 1 h / 160°C, 2 h / 250°C” or a “1 h/104°C, 5 h / 160°C, 2 h/250°C” cure cycle (Fig. 6). Samples of varying extents of cure were quenched in liquid nitrogen and subjected to STEM analysis. It is seen from Figure 8 that the differences in morphological developments is mainly brought about by the extended hold time at 160°C. The development of finer textures in the case of the “1 h/104°C, 5 h / 160°C, 2 h/250°C” cure cycle may thus be attributed to the

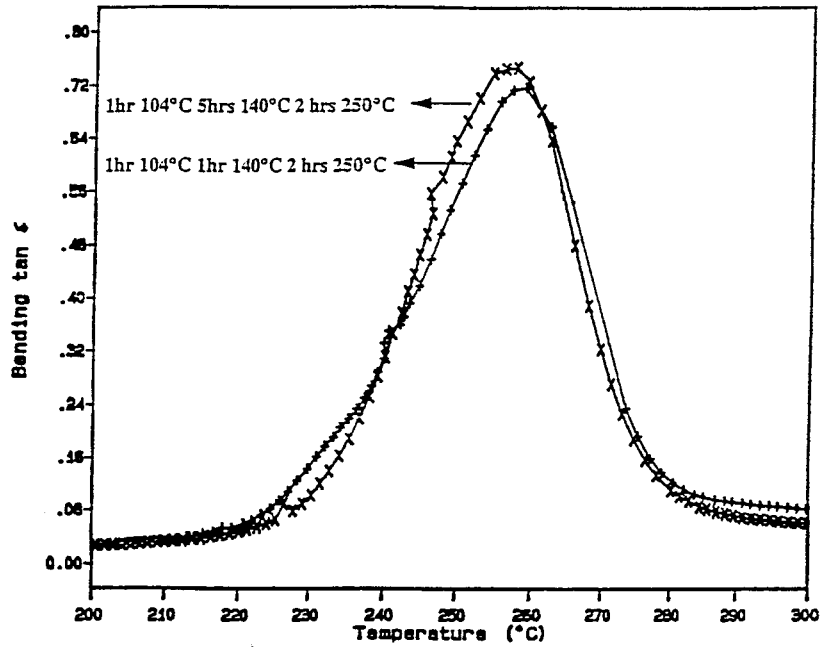


Figure 7 DMTA analyses at 0.1 Hz of 25 wt % 15K PPH-PSF-OH-modified networks: effect of cure cycle.

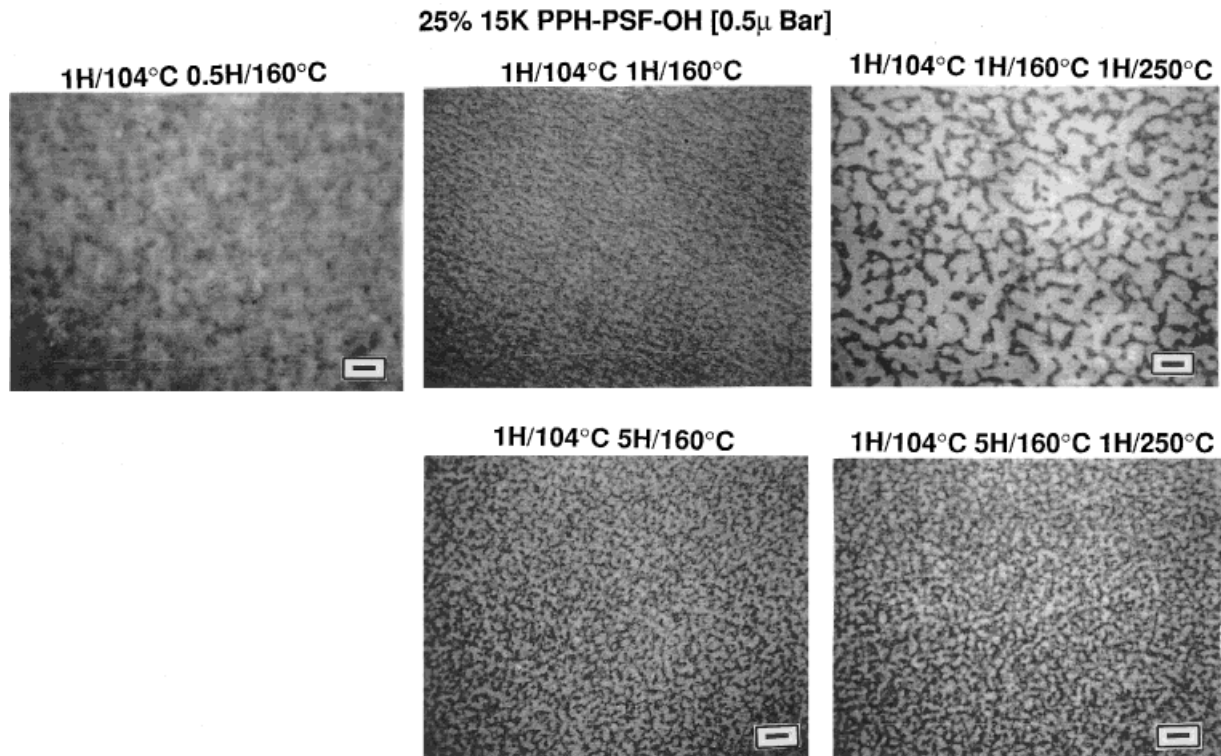


Figure 8 STEM of 25 wt % 15K PPH-PSF-OH-modified networks: morphological development as a function of cure. (Bar = 0.5 μ .)

slower cure (slower rate of conversion) as a result of the extended hold at 160°C relative to the "1 h/104°C, 1 h/160°C, 2 h/250°C" cure cycle.

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.

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. It is reasonable to expect that such gross macrophase-separated morphologies would likely result in no control whatsoever over the interface and the mechanical performance. Such gross macrophase-separated morphologies are less desirable from the point of performance control and prediction.

The heterophase morphological structure strongly influences the mechanical performance of the modified networks. In addition to factors such as backbone chemistry, molecular weight, and end functionality of the thermoplastic modifier, the generation of controlled microphase-separated morphologies, in the case of the reactive thermoplastic-modified systems, can also be effected by systematically varying thermal cure cycles. Such a cure cycle dependence of morphology was particularly demonstrated for the case of the 25 wt % 15K PPH-PSF-OH-modified networks. Morphologies that exhibited finer textures with respect to the sizes of the phase-separated domains translated into lower fracture toughness values.

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REFERENCES

1. D. A. Shimp, J. R. Christenson, and S. J. Ising, *Aro-Cy Cyanate Ester Resins: Chemistry and Properties*, Rhone-Poulenc, Inc., publication, 1989.
2. A. M. Gupta and C. W. Macosko, *Macromolecules*, **26**, 2455 (1993).
3. I. Hamerton, Ed., *Chemistry and Technology of Cyanate Ester Resins*, Chapman and Hall, 1994.
4. C. Arnold, P. Mackenzie, V. Malhotra, D. Pearson, N. Chow, M. Hearn, and G. Robinson, in *37th International SAMPE Symposium*, March 9–12, 1992, p. 128.
5. Z. Q. Cao, F. Mechin, and J. P. Pascault, *Polym. Mater. Sci. Eng. Prepr. (PMSE)*, **70**, 91 (1994).
6. G. R. Almen, *SAMPE Int. Tech. Conf.*, **21**, 304 (1989).
7. D. A. Shimp, F. A. Hudock, and W. S. Bobo, in *18th International SAMPE Technical Conference*, Oct. 7–9, 1986, p. 851.
8. J. C. Hedrick, A. Viehbeck, and J. T. Gotro, *ACS Polym. Prepr. Polym. Chem.*, **35**(1), 537 (1994).
9. S. A. Srinivasan and J. E. McGrath, *High Perform. Polym.*, **5**, 259–274 (1993).
10. S. A. Srinivasan and J. E. McGrath, *SAMPE Q., Apr.*, 25–29 (1993).
11. S. A. Srinivasan, S. S. Joardar, D. B. Priddy, Jr., T. C. Ward, and J. E. McGrath, in *Proceedings of the 39th International SAMPE Symposium and Exhibition*, Anaheim, CA, April 1994, p. 60.
12. S. A. Srinivasan, S. S. Joardar, D. B. Priddy, Jr., T. C. Ward, and J. E. McGrath, in *Proceedings of the Materials Research Society*, Spring Meeting, San Francisco, CA, April 1994, p. 705.
13. J. Cartwright, S. A. Srinivasan, J. E. McGrath, A. Loos, D. Hood, D. Kranbeuhl, and T. C. Ward, in *Proceedings of the 17th Annual Meeting of the Adhesion Society*, Feb. 20–23, 1994, p. 62.
14. D. S. Porter, J. M. Brown, S. A. Srinivasan, T. C. Ward, and J. E. McGrath, in *American Chemical Society, Polymer Materials: Science and Engineering (PMSE) Preprint, Symposium on Cyanate Ester Networks*, 1994, Vol. 71, p. 817.
15. D. R. Hahn, S. S. Joardar, S. A. Srinivasan, and T. C. Ward, in *American Chemical Society, Polymer Materials: Science and Engineering (PMSE) Preprint, Symposium on Cyanate Ester Networks*, 1994, Vol. 71, p. 756.
16. D. Hahn, S. Joardar, S. Srinivasan, and T. C. Ward, *Polym. Mat. Sci. Eng. Prepr.*, **69**, 74 (1993).
17. J. M. Brown, S. Srinivasan, A. Loos, T. C. Ward, D. Kranbeuhl, and J. E. McGrath, *Polymer*, **37**(9), 1691–1696 (1996).
18. J. L. Hedrick, I. Yilgor, G. L. Wilkes, and J. E. McGrath, *Polym. Bull.*, **13**, 201 (1985). J. L. Hedrick, PhD Dissertation, Virginia Tech, 1985; J. L. Hedrick, I. Yilgor, M. Jurek, J. C. Hedrick, G. L. Wilkes, and J. E. McGrath, *Polym. (Lond.)*, **32**(11), 2020–2032 (1991).

19. M. J. Jurek and J. E. McGrath, *Polymer*, **30**, 1552 (1989).
20. C. D. Smith, PhD Dissertation, Virginia Polytechnic Institute and State University, 1991; *High Perform. Polym.*, **4**, 211 (1991).
21. G. D. Lyle, J. S. Senger, D. H. Chen, S. Kilic, S. D. Wu, D. K. Mohanty, and J. E. McGrath, *Polymer*, **30**, 978 (1989).
22. J. L. Hedrick, D. K. Mohanty, B. C. Johnson, R. Viswanathan, J. A. Hinkley, and J. E. McGrath, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 287 (1986).
23. A. J. Wnuk, T. F. Davidson, and J. E. McGrath, *Appl. Polym. Symp.*, **34**, 89–101 (1978).
24. D. A. Shimp, J. R. Christenson, and S. J. Ising, *AroCy Cyanate Ester Resins: Chemistry and Properties*, Rhone-Poulenc, Inc., publication, 1989.
25. C. A. Fyfe, J. Niu, S. J. Rettig, N. E. Burlinson, C. M. Reidsema, D. W. Wang, and M. Poliks, *Macromolecules*, **25**, 6289 (1992).
26. A. M. Gupta and C. W. Macosko, *Macromolecules*, **26**, 2455 (1993).