Polymer Vol. 37 No. 9, pp. 1691–1696, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

Production of controlled networks and morphologies in toughened thermosetting resins using real-time, *in situ* cure monitoring

J. M. Brown
Hughes Missile Systems Co., PO Box 11337, Bldg 805 Mail Stop D4, Tucson, AZ 85734-1337, USA

and S. Srinivasan, A. Rau, T. C. Ward*, J. E. McGrath and A. C. Loos
National Science Foundation Center for High Performance Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0344, USA

and D. Hood and D. E. Kranbeuhl
College of William and Mary, Williamsburg, VA 23187-8795, USA
(Received 18 January 1995; revised 17 August 1995)

Based on knowledge of the chemical reactions and morphology, significant changes can be made in the morphology of a toughened dicyanate thermosetting resin through the intelligent manipulation of the cure cycle and real-time knowledge of the conversion of the system. Fourier transform near infra-red spectroscopy using fibre-optic sensors was employed to follow such reactions. Various cure cycle changes resulted in similar degree of cure, thermal stability and solvent resistance, but yielded a 20% change in neat resin toughness associated with the morphologies. The morphological variety was shown not only to occur within reasonable cure cycle variations for neat resin, but were also induced through a processing change in a graphite-reinforced composite containing this resin. Design of custom or gradient morphologies to provide specific mechanical properties is now feasible with this technology. These same approaches could be adapted to the custom manufacture of optical and/or damping properties. This manipulation is not limited to the processing of toughened thermosetting resins. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cyanate esters; Fourier transform near infra-red spectroscopy; gradient morphologies)

INTRODUCTION

Composite matrix resins are often multicomponent formulations requiring a number of complex chemical and physical changes to occur in the proper sequence to produce the appropriate mechanical properties. What seems a simple issue of processing may involve four or five different, possibly competing reactions, phase separation (to toughen) and the transformation of the low-molecular-weight liquid material to a glassy solid. Changing the cure profile of such a thermosetting resin can drastically alter the properties through changes in the network and/or in the morphology. This has been demonstrated qualitatively for toughened epoxies but is not so well demonstrated for other reaction chemistries and tougheners. This paper summarizes in part recent investigations of these phenomena for polysulfone cyanate ester based materials[1,2].

A Fourier transform near infra-red (*FT*n.i.r.) fibre-optic conversion sensor can be used alone or, as demonstrated below, *in situ* to provide simultaneous, real-time, complementary chemical information to the physical state data obtained from an implantable dielectric sensor. Information on phase separation, vitrification, density and temperature were accessible from peak shifts and changes in the peak areas in the *FT*n.i.r. spectra. Multiplexing the fibre-optic signal to a visible detector provided further information, especially pertaining to phase separation. These sensor combinations have great potential for use with intelligent processing systems.

Changing the cure profile of a thermosetting resin can drastically alter its properties through changes in the network and/or the morphology. There is evidence[3,4] that the time–temperature pathways affect the properties of the untoughened systems even when reacted to the same level of conversion. Such effects are much more dramatic for toughened systems where a second phase develops as the initially homogeneous resin cures. As shown by Gillham and co-workers[5-8], Butta *et al.*[4], Montarnal *et al.*[9] and others[10-24], for rubber-toughened epoxies, a 0–50% change in mechanical properties, such as fracture toughness and impact strength, can result from changes in the time–temperature curing profile. Researchers have produced changes in morphology,

---

* To whom correspondence should be addressed

dynamic mechanical behaviour, Young's modulus, elongation at break, T-peel strength, yielding behaviour, lap shear strength, failure mode and damping behaviour of toughened epoxies, for example, by changing the cure cycle[3-27]. Microwave cavities have been applied[25-27] to trap novel morphologies by accelerating the associated chemical reactions. Yamanaka and co-workers[17,18] suggested that a 'controlled' morphology with novel properties could be obtained thermally through the proper balance of chemical and physical changes.

Yamanaka and Inoue[17], working with a poly(ethersulfone)-toughened aromatic-diamine-cured epoxy which phase-separated by spinodal decomposition, produced several novel two-phase morphologies. As background, a lower critical solution temperature (*LCST*) behaviour had been reported for the bisphenol-A based poly(hydroxy ether) known as 'phenoxy' and poly(ethersulfone) (PES). These authors expected this sort of phase separation for epoxy with PES. With a formulation that displayed *LCST* in the phase diagram, starting at a point in the homogeneous region of the phase diagram and heating, the resin phase separation developed. Beginning at a point in the one-phase region, and now in a reactive system, phase separation occurred as the reaction proceeded. The glass transition temperature (T_g) of the resin increased as the reaction proceeded, trapping the morphology. Examination of fracture surfaces showed 'interconnected globules' resulting from spinodal decomposition followed by ripening. These morphologies resulted in increases in peel and shear strength over the untoughened epoxies. Yamanaka and Inoue comment that the co-continuous structure associated with spinodal decomposition would give a high initial modulus, high strain at break and good strain recovery[17].

Various temperature ramps and isothermal curves have been evaluated[17] with respect to trapped morphologies. Slower temperature increases produced smaller domain sizes (or periodic distances). The sizes were also reduced by lower temperature isothermal treatments. To obtain a 'fine-grained' morphology in a resin undergoing spinodal decomposition, the authors recommended that 'coarsening of the phase-structure should be suppressed by network formation in the early stages of spinodal decomposition' by curing as close to T_g as possible. Near T_g, the reaction rate greatly exceeds the phase-separation rate.

Yamanaka *et al.*[18] proposed that the dispersed spherical particles often observed with rubber-toughened epoxies could be generated from spinodal decomposition rather than binodal decomposition. Using a combination of a rapid curing agent, low temperature cure and an ATBN (acid terminated butadiene nitrile) rubber, they produced a co-continuous morphology indicative of gelation during the early stages of a spinodal decomposition. This morphology yielded interesting peel strength and damping properties.

Untoughened systems can be changed by contrasting cure cycles as demonstrated by Brett[3] for a diamine-cured epoxy. After subjecting the resin to various cure cycles (ramps and/or dwells), it was reported that isocure states did not necessarily yield the same adhesive lap shear strength values. He attributed these differences to a preferential selection of one of the many curing reaction or paths to similar final cure conversions. This condition may exist for many systems since a number of resins have multiple curing paths. In this present study, the cyanates have been selected to reduce the possibility of competitive reactions. The cyanate reaction is not perfect, but has at least 85% (often better than 95%) conversion to triazine crosslinks[28,29].

The network and morphological possibilities discussed above are usually not considered in conventional (or in intelligent) processing. Resins typically undergo a thermal cycle which is optimized to produce certain macroscopic mechanical (toughness, modulus) or thermal properties (such as T_g), ignoring to some extent the chemical and morphological changes that contribute to these properties. Not all of the reported time–temperature pathway options are intentional. Loos and co-workers[30,31] demonstrated that the temperature inside a thick graphite-reinforced composite panel was significantly different from the intended autoclave cycle. This was due to heat transfer from the outside and the exothermic nature of most thermosetting reactions. It is not unreasonable,

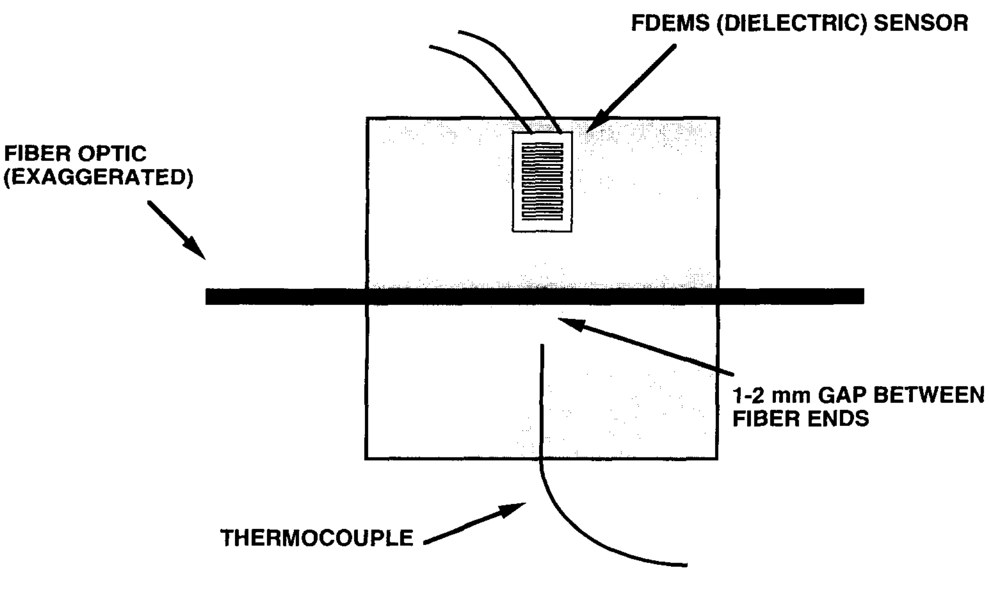


Figure 1 Resin casting mould adapted for fibre optics

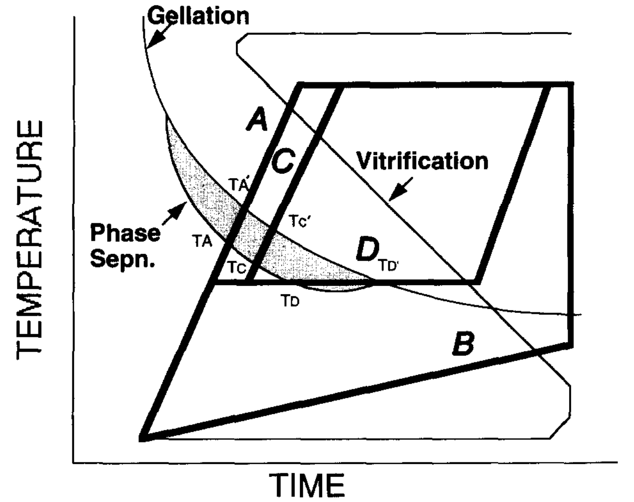


Figure 2 Basic TTT diagram for toughened resins[34] with superimposed processing cycles

based on the above, to suppose that there may be a 10–30°C temperature differential across a composite panel or an adhesive joint at some time during the cure cycle. Such conditions can lead to widely varying materials as demonstrated below.

EXPERIMENTAL

Approximately 20 to 25 g of a toughened cyanate formulation[2] composed of the dicyanate of bisphenol-A (BADCy) with 250 ppm aluminium acetyl acetonate (AlAcAc) and 2 pph nonyl phenol, with or without 25% of a reactive thermoplastic (15K PPES-OH), was mixed at 104°C and then subjected to various time/temperature profiles. The 15K PPES-OH was a hydroxyl-terminated poly(ethersulfone) with number-average molecular weight of 15 000 g mol^{-1}. The control cure cycle included a 2°C min^{-1} ramp to 250°C and a 2.25 h postcure. Intermediate isothermal stages at 135, 150, 180 or 200°C were applied as noted to vary curing kinetics relative to the control. The specimens were held at these temperatures to a relative conversion of either 30 or 60%, then ramped in temperature to the postcure.

Conversion was monitored *in situ* during the specimen cure by a Nicolet model 800 FTIR spectrometer equipped with a fibre-optic adapter and low hydroxyl silica fibre optics (Polymicro Technologies). A special aluminium mould with a groove (0.38 mm wide by 0.5 mm deep) in the bottom and small openings in the side was machined (see *Figure 1*) to allow the insertion of the fibre-optic sensor for monitoring the triazine peak in the near infrared region at 4625 cm^{-1} (as described in ref. 1). This configuration was alternately used with an optometer (United Technology) with a 650 nm detector to monitor light intensity, and was used with a Dek Dyne (FDEMS) cure monitoring system to simultaneously monitor chemical conversion and dielectric properties (ϵ' and ϵ'').

No side reactions were detected in the near infra-red spectrum for this system. Using the aromatic ring stretch as a reference, a relative conversion (denoted as α) was calculated based on a normalized triazine peak[1]. A software program allowed real-time collection of spectra, baseline correction, integration of aromatic ring and triazine ring stretches, ratioing of peaks and real-time calculation of a relative degree of conversion.

Microtomed samples[2], stained with ruthenium tetroxide, were evaluated by scanning transmission electron microscopy at 2500× magnification.

RESULTS AND DISCUSSION

The cured resin chosen as a model in this study had been

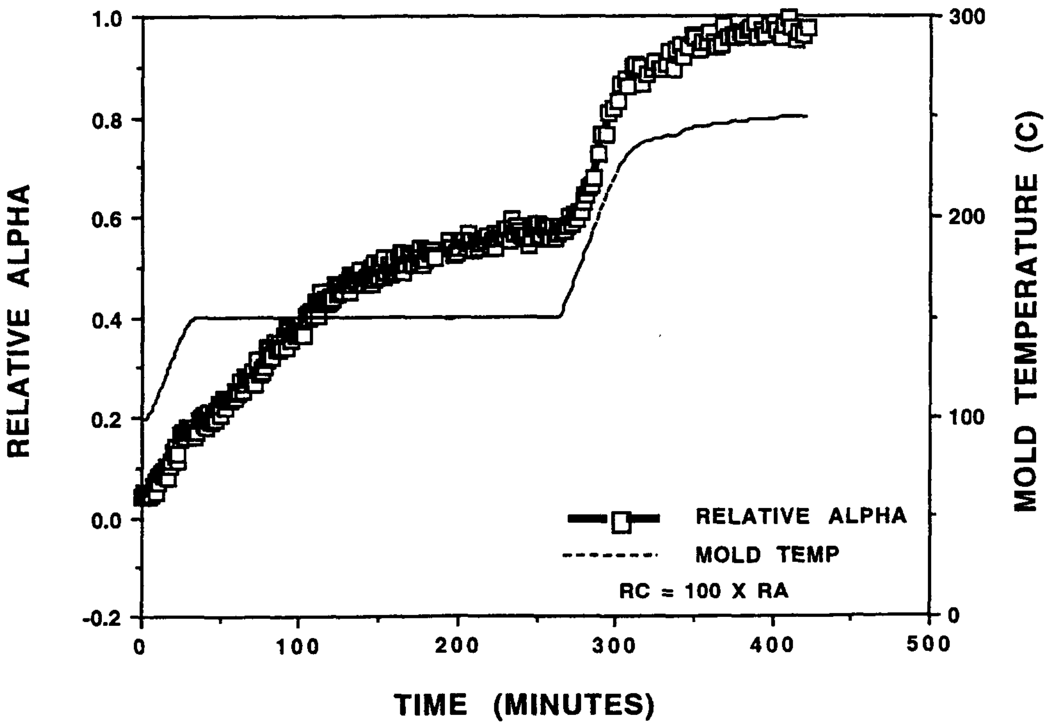
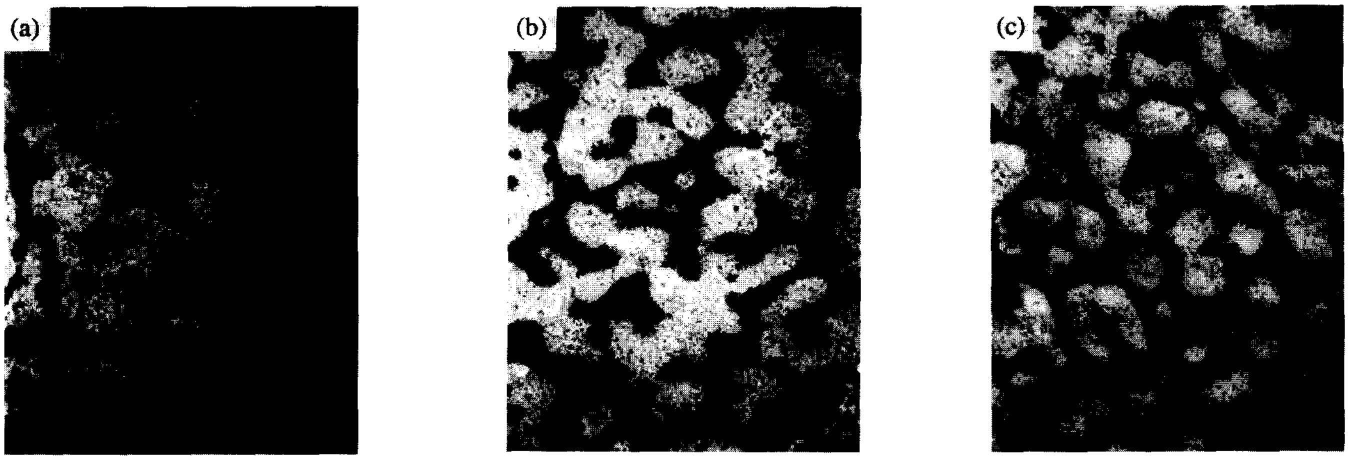


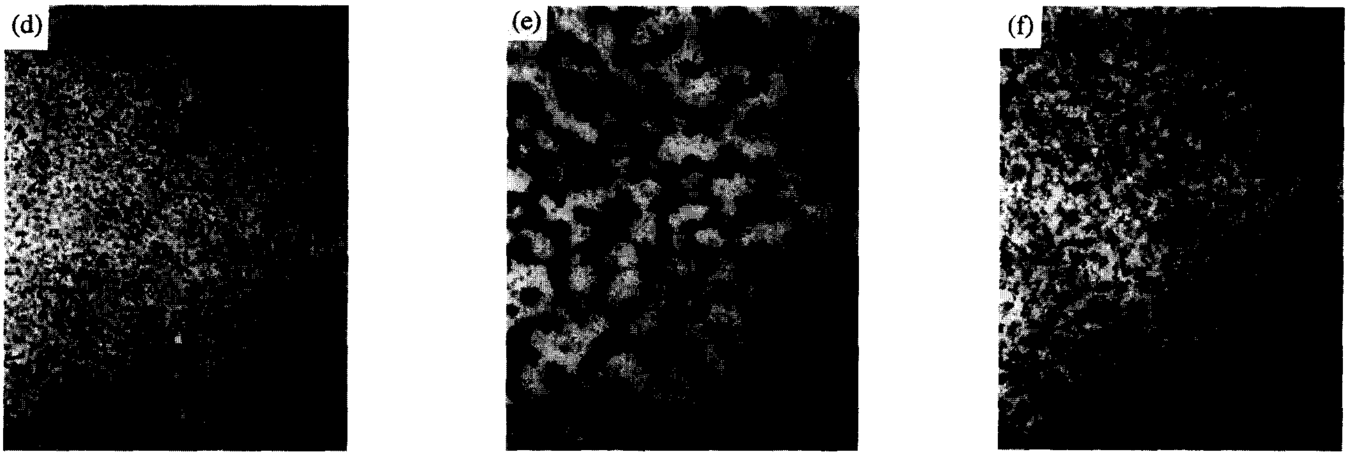
Figure 3 Real-time monitoring of relative degree of cure (α_r) during the cure of resin castings



1 C/min to 250°C.
No intermediate hold.
Postcure 2.25 hrs. at 250°C.

2 C/min to 150°C.
Hold 150°C until RC = 30%.
Postcure 2.25 hrs. at 250°C.

2 C/min to 135°C.
Hold 135°C until RC = 30%.
Postcure 2.25 hrs. at 250°C.



2 C/min to 135°C.
Hold 135°C until RC = 60%.
Postcure 2.25 hrs. at 250°C.

2 C/min to 150°C.
Hold 150°C until RC = 30%.
Postcure 2.25 hrs. at 250°C.

2 C/min to 150°C.
Hold 150°C until RC = 60%.
Postcure 2.25 hrs. at 250°C.

Figure 4 Morphologies resulting from interactive cure cycle modifications

shown by Srinivasan[2] to possess a phase-separated interpenetrating morphology having a characteristic dimension of the order of 1 μm. Such results are associated with kinetic and thermodynamically controlled phenomena during spinodal decomposition. In order to change the morphology of the resin, two conditions needed to be satisfied[5-8]. The resin needed to be heated to a controlled lower temperature where the mobility was low (and the viscosity high) and then to be maintained at that condition until gelation. Cyanate resins have been empirically observed to gel at 60–65% conversion[28,32,33]. *Figure 2* shows a time–temperature–transformation (TTT) diagram[34] with four processing pathways, designated A, B, C and D, superimposed. Pathway A cuts diagonally across the TTT diagram from a low temperature to a high temperature. This would correspond to a +2°C min^{-1} control ramp and yield a heterogeneous morphology. At some temperature T_A, phase separation would begin. Phase separation terminates at T_A^1. Pathway B represents a ramp up to a constant temperature that is low enough so that phase separation does not occur prior to gelation. The resulting morphology would be homogeneous. Path C or D would be typical of most of the cure cycles used in this study. In cycle C, a very short dwell at the initial cure temperature would not be sufficient to induce phase separation. Phase separation would begin at temperature T_C in the subsequent linear ramp of temperature. In the fourth cycle (path D) intermediate temperatures occur, but the isothermal dwell is long enough for phase separation and trapping of the morphology by gelation or vitrification of the resin. Subsequent temperature ramps should not provide sufficient mobility to change this morphology.

A processing cycle in which temperature was ramped by 2°C min^{-1} to 250°C followed by 2.25 h at 250°C was selected as a control cycle[2]. Isothermal dwells at 135, 150, 180 or 200°C were maintained to a predetermined level of conversion (30 or 60%) based on the real-time conversion data from the *FT*n.i.r. fibre-optic sensor in the mould, and then allowed to finish the cure cycle. Real-time relative conversion (α = conversion/100) data are shown in *Figure 3* for one of the cure cycles.

A scanning transmission electron photomicrograph illustrating the morphology for the (2°C min^{-1}) control cycle is shown in *Figure 4a*. In the photo, the black represents the (stained) thermoplastic-rich areas. The particles were irregular, approximately 0.5–1.0 μm in size, well phase-separated and highly interlocked, no phase appearing to be continuous. The morphologies resulting from additional cure cycles are shown in *Figures 4b* to *d*; all photos are at the same magnification. The lower levels of conversion (30%), such as in path C on the TTT diagram, had little effect on the morphology for the low temperature staging. These low levels of conversion were inadequate either to induce phase separation or to trap the finer microstructures. At 60% conversion, dramatic morphology differences were observed. The resin produced by the (ramped) control cycle was visibly turbid, having well phase-separated particles the size of the wavelength of visible light. Isothermal cures to 60% conversion between 135 and 180°C trapped a very fine, mixed-phase morphology which produced a transparent resin. The 135°C isothermal dwell did not produce a well-defined structure. At 150 and 180°C, the phase regions were slightly larger (approximately 0.15 μm) and better defined than those at 135°C. The morphologies trapped at 60% conversion for 135, 150 and 180°C are consistent with the early stages of spinodal decomposition.

At 180°C (results not shown), there was less difference between the morphologies at 30 and 60% conversion, probably due to the very rapid reaction at this temperature. At 200°C (*Figure 4b*), the morphology of the control specimen was again found. Visible fibre-optic light transmission data during the 2°C min^{-1} control cycle showed a dramatic decrease in transmission between 180 and 200°C, as would be expected from scattering due the formation of distinct, phase-separated particles of the size of the wavelength of light[1]. Both the control and the 200°C isothermal resin castings were visibly turbid. While the earliest part of spinodal phase separation for the control morphology could not be seen with the light transmission method, between 180 and 200°C the two phases became distinct enough to be observed. Simultaneous complementary *FT*n.i.r. fibre-optic conversion data and dielectric loss factor and permittivity were obtained for two of the cure cycles (*Figure 5*) to further explore these phenomena.

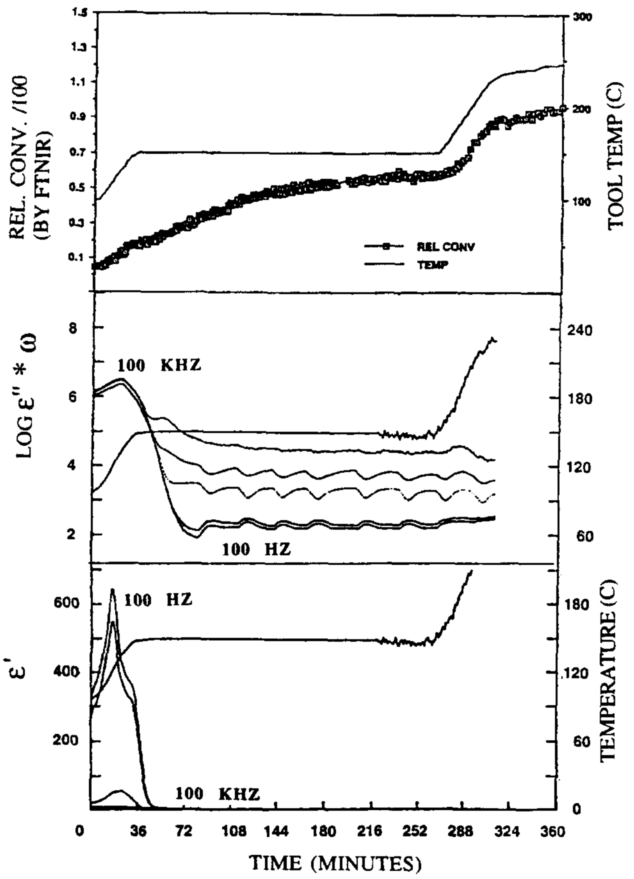


Figure 5 Simultaneous fibre-optic conversion and dielectric loss factor during cure

Despite the significant differences in morphology, all cure cycles produced polymers having similar thermal properties. Assuming no trapped cyanate reactive groups, all specimens were found to have achieved >98% conversion by differential scanning calorimetry (d.s.c.), with no significant differences between the cure cycles. Likewise, weight losses in air and storage moduli for all cycles were similar.

The natural question at this point is whether these various cyanate ester morphologies exhibit different physical properties. To evaluate the effects of the morphology produced in these studies, Srinivasan[2] made a series of fracture toughness (K_{IC}) specimens using isotherms at 140, 160 and 180°C. The morphologies produced confirmed the trends originally observed in the instrumented cure cycles of this current paper. The toughness, as measured by K_{IC}, dropped 20% for the finer morphologies produced by the isothermal temperatures.

Although these large changes in morphology seem to result in only moderate changes in some of the mechanical and thermal properties, durability issues have not been addressed. Based on the changes in morphology induced in these processing studies, a series of double cantilever beam durability tests to determine the effects of changes in morphology on durability is underway.

Other researches have been processing graphite (AS4) fibre-reinforced composite panels using the 25% model thermoplastic toughened cyanate for mechanical testing purposes and modelling. The processing of these laminates had been optimized for consolidation and fibre

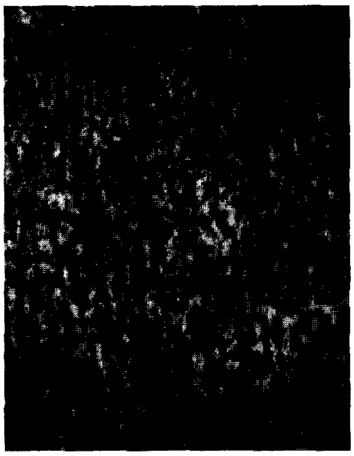

Morphology of composite panel with 160°C processing hold.

Figure 6 Morphologies of a composite panel with a 160°C dwell volume (60–65%) by the incorporation of an isothermal stage in the cure at 160°C for 1.5 h[34]. Based on the resin studies, one would expect that the processing dwell would result in a smaller, mixed morphology and an associated drop in properties related to toughness. Resin-rich areas of a 16-ply quasi-isotropic lay-up panel processed in this manner were examined by staining and transmission electron microscopy (*Figure 6*). The black bar is 0.5 μm. The composite panel showed a very fine, small ($< 0.2\,\mu$m) morphology that would be expected to result from the intermediate temperature isotherm to gelation.

CONCLUSIONS AND SUMMARY

Processing cycles, monitored with *in situ*, real-time *FT* n.i.r. fibre optics, were used to control network formation in a reactive thermoplastic-toughened cyanate. The cures trapped a series of novel morphologies by gelation. Extremes in morphologies were produced within reasonable cure cycle variations. The same sort of changes in morphologies were found in a composite laminate which had an intermediate temperature isothermal stage introduced for processing purposes. Samples had similar degrees of cure (based on d.s.c.), thermo-oxidative stability, dynamic modulus, and T_g. A study is underway to determine if these changes in morphology have any affect on the long-term durability of adhesive joints. The potential exists to produce materials with controlled microstructures which may result in customized mechanical, optical and perhaps fatigue properties.

ACKNOWLEDGEMENT

The majority of this work was funded by the National Science Foundation Science and Technology Center: High Performance Polymeric Adhesives and Composites (DMR-9120004).

REFERENCES

1 Brown, J. *Dissertation*, Virginia Polytechnic Institute and State University, 1994

2 Srinivasan, S. *Dissertation*, Virginia Polytechnic Institute and State University, 1994

3 Brett, C. L. in 'Adhesion—3' (Ed. K. W. Allen), Applied Science Publishers, London, 1977, pp. 53–64

4 Butta, E., Levita, G., Machetti, A. and Lazzerri, A. *Polym. Eng. Sci.* 1986, **26**, 63

5 Manzione, T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 889

6 Manzione, T., Gillham, J. K. and McPherson, C. A. *J. Appl. Polym. Sci.* 1981, **26**, 907

7 Chan, L. C., Gillham, J. K., Kinloch, A. J. and Shaw, S. J. in 'Rubber-Modified Thermoset Resins' (Eds C. K. Riew and J. K. Gillham), Adv. Chem. Ser. 208, American Chemical Society, Washington, DC, 1983, pp. 235–260

8 Chan, L. C., Gillham, J. K., Kinloch, A. J. and Shaw, S. J. in 'Rubber-Modified Thermoset Resins' (Eds C. K. Riew and J. K. Gillham), Adv. Chem. Ser. 208, American Chemical Society, Washington, DC, 1983, pp. 2261–2279

9 Montarnal, S., Pascault, J. P. and Sautern, H. in 'Rubber-Toughened Plastics' (Ed. C. K. Riew), Adv. Chem. Ser. 222, American Chemical Society, Washington, DC, 1989

10 Williams, R. J. J., Borrajo, J., Adabbo, H. E. and Rojas, A. J. in 'Rubber-Modified Thermoset Resins' (Eds C. K. Riew and J. K. Gillham), Adv. Chem. Ser. 208, American Chemical Society, Washington, DC, 1983, pp. 195–213

11 Vasquez, A., Rojas, A. J., Adabbo, H. E., Borrajo, R. and Williams, R. J. J. *Polymer* 1987, **28**, 1156

12 Borrajo, J., Riccardi, C. C., Moschiar, S. T. and Williams, R. J. J. in 'Rubber-Toughened Plastics' (Ed. C. K. Riew), Adv. Chem. Ser. 222, American Chemical Society, Washington, DC, 1989

13 Verchere, D. H., Pascault, J. P., Moschiar, S. M., Riccardi, C. C. and Williams, R. J. J. *ACS PMSE Preprints* 1990, **63**, 99

14 Verchere, D., Pascault, J. P., Sautereau, H., Moschiar, S. M., Riccardi, C. C. and Williams, R. J. J. *J. Appl. Polym. Sci.* 1991, **42**, 701

15 Moschiar, S. M., Riccardi, C. C., Williams, R. J. J., Verchere, D., Sautereau, H. and Pascault, J. P. *J. Appl. Polym. Sci.* 1991, **42**, 717

16 Verchere, D., Pascault, J. P., Sautereau, H., Moschiar, S. M., Riccardi, C. C. and Williams, R. J. J. *J. Appl. Polym. Sci.* 1991, **43**, 293

17 Yamanaka, K. and Inoue, T. *Polymer* 1989, **30**, 662

18 Yamanaka, K., Takagi, Y. and Inoue, T. *Polymer* 1989, **30**, 1839

19 Ohnaga, T., Maruta, J. and Inoue, T. *Polymer* 1989, **30**, 1845

20 Hsich, H. S.-Y. and Howard, W. J. *ACS PMSE Preprints* 1990, **63**, 127

21 Hsich, H. S.-Y. *Polym. Eng. Sci.* 1989, **30**, 493

22 Hsich, H. S.-Y. *J. Mater. Sci.* 1990, **26**, 1568

23 Hsich, H. S.-Y. *J. Mater. Sci.* 1991, **26**, 3209

24 Hsich, H. S.-Y. *Adv. Polym. Technol.* 1990, **10**, 185

25 Hedrick, J. L. *Dissertation*, Virginia Polytechnic Institute and State University, 1985

26 Liptak, S. C. *Dissertation*, Virginia Polytechnic Institute and State University, 1993

27 Liptak, S. C., Wilkinson, S. P., Hedrick, J. C., Ward, T. C. and McGrath, J. E. in 'Radiation Effects on Polymers' (Eds R. L. Clough and S. W. Shalaby), American Chemical Society, Washington, DC, 1991, pp. 364–383

28 Gupta, A. M. and Macosko, C. W. *Makromol. Chem., Macromol. Symp.* 1991, **45**, 105

29 Fyfe, C. A., Niu, J., Retting, S. J., Burlison, N. E., Reidsema, C. W., Wand, D. W. and Poliks, M. *Macromolecules* 1992, **25**, 6289

30 Loos, A. and Springer, G. *J. Compos. Mater.* 1983, **17**, 135

31 Loos, A. and Freeman, W. T. in *ASTM STP 873*, American Society for Testing and Materials, Philadelphia, PA, 1985, pp. 1119–1130

32 Chen, Y.-T. and Macosko, C. W. 24th International SAMPE Technical Conference (Preprints), Corvina, CA, October 1992

33 Gupta, A. M. and Macosko, C. W. *Macromolecules* 1993, **26**, 2455

34 Wisanrakkit, G. and Gillham, J. K. in 'Polymer Characterization' (Eds C. D. Craver and T. Provder), Adv. Chem. Ser. 227, American Chemical Society, Washington, DC, 1990, pp. 143–166

35 Rau, A. Virginia Polytechnic Institute and State University, to be published