Phase structure and toughening mechanism of a thermoplastic-modified aryl dicyanate

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A high temperature thermosetting aryl dicyanate resin was modified with thermoplastic polysulfone and/or poly(ether imide) at various compositions. Differential scanning calorimetry was used to characterize the phase behaviour, while the morphologies and continuities of the thermoplastic/dicyanate networks were investigated by using dynamic mechanical analysis, scanning electron microscopy, fracture toughness testing, and solvent sorption studies. The phase structure was found to change from a thermosetting continuity to a co-continuity of both thermoplastic and thermosetting domains. The mechanical and physical properties of the modified polycyanates exhibited a step change at the shift of the phase structure.

(Keywords: phase; fracture toughness; continuity)

INTRODUCTION

Dicyanate resins have been used as matrix materials for glass or Aramid fibre reinforced circuit boards in electronic applications since 1968 owing to their low dielectric constants and high thermal stabilities[1]. Recent studies have demonstrated that crosslinked polycyanates provide unique features and can be considered as candidate matrices for advanced composites in demanding environments[2–8]. The cured dicyanates, or polycyanates, all possess high glass transition temperatures (250–280°C), low water/moisture sorption, and excellent processability and compatibility with carbon fibre[2]. In addition, the cyanate resins are also well studied in terms of their cure kinetics[9–11]. Generally, dicyanate resins possess a processability comparable to most epoxy or bismaleimide resins, while crosslinked polycyanates exhibit higher T_g values and fracture toughnesses than most epoxies or bismaleimides.

Thermosetting resins are generally brittle and difficult to toughen. Rubber toughening has been well studied for many epoxy systems. However, rubber toughening results in depression of the glass transition temperature, modulus and thermal stability, especially at high rubber contents. The fracture toughnesses of epoxies have been shown to be moderately improved by modification with thermoplastics[12]. More recently, an effective technique of toughening epoxy resins has been demonstrated by incorporating both rubber and thermoplastics[13]. Owing to the reactive nature, the morphologies of the thermoplastic-modified thermosets are more difficult to predict than those of thermoplastic blends. Most non-reacting thermoplastic blends exhibit equilibrium or near-equilibrium phase behaviour with a continuous/discontinuous phase morphology. Normally, for rubber-modified or thermoplastic-modified epoxies, the major component forms the continuous phase and the minor component forms the discontinuous phase. For thermoplastic-modified epoxy systems, the fracture toughness is often dependent on the domain size of the discontinuous phase[12,13].

The feasibility of improving the fracture toughness of the aryl dicyanate resin was investigated by incorporating high T_g thermoplastics, such as polysulfone (PSu) and/or poly(ether imide) (PEI). In this study, the factors that might influence the morphology of the thermoplastic-modified dicyanate ester were examined. Attempts were made to establish relationships between morphology and fracture toughness in the heterogeneous, thermoplastic-modified, thermosetting aryl dicyanates. The phenomenon of phase separation and the formation of domain structures in the cured networks are discussed.

EXPERIMENTAL

Materials

The aryl dicyanate resin used was a bisphenol-E

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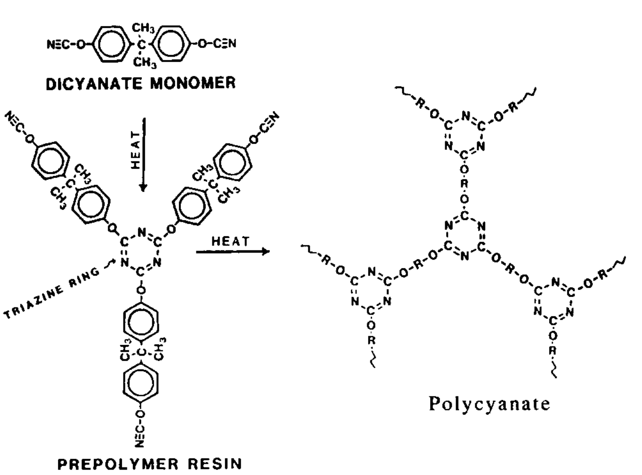

Scheme 1 Schematic showing the cyclotrimerization of the thermosetting aryl dicyanate resin to give the crosslinked polycyanate

dicyanate (BEDCy) of high purity supplied by Hi-Tek Polymers Inc., USA (currently a division of Rhone–Poulenc Inc.). As a result of asymmetry in its molecular structure, the bisphenol-E dicyanate (BEDCy) does not easily crystallize and exists as a monomeric, low viscosity liquid resin. The cyclotrimerization of the thermosetting aryl dicyanate resin to give the crosslinked polycyanate is shown in *Scheme 1*. The cure reactions of dicyanate resins produce triazine rings (six-membered rings of alternating C–N bonds) which are thermally stable. After thermosetting, all the triazine rings are interconnected (crosslinked) on the carbon atoms by molecular chains of –ORO– to form a three-dimensional network.

Two amorphous, thermoplastic polymers were used as toughening modifiers for the dicyanate resin. The thermoplastics were polysulfone (PSu) (Amoco UDEL® P1700) with a T_g of 185°C and poly(ether imide) (PEI) (GE Ultem 1000) with a T_g of 210°C. They were used as received. The PEI[12] had $M_n = 12\,000$ and $M_w = 30\,000$.

Sample preparation

The mixtures of the thermoplastics with the BEDCy dicyanate resin were prepared using the melt-mixing technique. The dicyanate resin was first heated to about 160°C before the thermoplastic (in a fine powder form) was added slowly with continuous stirring to ensure a uniform temperature and faster dissolution. Mixing at temperatures as high as 160°C was not a concern since the cure reactions of the dicyanate resin require a catalyst. In the absence of the catalyst, the cure reactions of the dicyanate resin did not progress at any significant rate even at the blending temperatures as high as 160°C. Mixing was judged complete when the mixture became transparent (the opaqueness caused by entrapped air bubbles should not be confused with incomplete dissolution). The blending/dissolution process took approximately 30 min at 160°C. At the end, a catalyst was added to the thermoplastic/resin mixture at about 2 wt% of the mixture. The catalyst as supplied was a 20/1 mixture of nonylphenol with copper acetylacetonates. Stirring was continued for 2 min following addition of the catalyst, and the mixing was judged complete. Subsequently, the mixture was transferred to a vacuum oven (preset at about 150°C) to remove air/vapour bubbles from the mixture. The degassing took an additional 15 min at 150°C. After proper degassing, all uncured thermoplastic/dicyanate mixtures were transparent and appeared to be homogeneous.

It should be noted that the melt-mixing technique was applicable to the preparation of mixtures of the thermoplastic with the dicyanate resin only when the content of the thermoplastic in the mixture was less than or equal to 20 wt%. The viscosity increased rapidly at increased loadings of the thermoplastic. The general guideline was that 20 wt% of the thermoplastic in the dicyanate resin represented the approximate maximum loading achievable by the melt-mixing technique. Additionally, 20 wt% of thermoplastic in the dicyanate resin also represented the maximum viscosity for feasible prepregging operations. At a thermoplastic content greater than 20 wt%, the high viscosity of the blended thermoplastic/dicyanate mixture made it extremely difficult to impregnate completely the carbon fibre tows at most prepregging temperatures (150°C or below).

For the differential scanning calorimetry (d.s.c.) studies, only relatively small quantities of the specimens were required. Consequently, a solution-mixing technique (using methylene chloride) was used to prepare thermoplastic/dicyanate mixtures containing higher thermoplastic loadings between 20 and 80 wt%. Degassing of a small quantity of resin mixture could be completed in a short time before the resin mixture aged to the gel point. The main obstacle with the solution-mixing technique was the extreme difficulty in thoroughly removing the residual solvent or solvents from the mixture (by degassing) before the gel point was reached. Consequently, the solution-mixing technique could not be used if large quantities of the thermoplastic/dicyanate mixture were required to prepare, for example, samples of neat-resin plaques or prepregging for carbon fibre laminates.

After mixing, the resin mixtures were cast into glass moulds which had been treated with a release agent. Cure cycles for the thermoplastic/dicyanate mixtures included 2–3°C min^{-1} heating to 177°C with an isothermal hold for 2 h at 177°C. The neat-resin plaques were post-cured at 220°C for 2 h. Post-curing of the dicyanate resins is usually necessary to develop optimal mechanical properties[3]. After full cure, the clear, liquid thermoplastic/dicyanate mixtures were turned into crosslinked thermoplastic/thermoset networks with a seemingly heterogeneous morphology as evidenced by the cloudy appearance. Heterogeneity was observed for all the cured, thermoplastic-modified polycyanate networks.

Apparatus and procedures

Thermal analysis. Differential scanning calorimetry (DuPont DSC-910) was used to measure the extents of the residual curing reactions, and also to determine the glass transition temperatures of the cured matrices. The heating rate used was 5°C min^{-1} in all d.s.c. tests.

Dynamic mechanical analysis (d.m.a.) was performed on a DuPont DMA-983 coupled to a DuPont TA-2000 computer system for data acquisition and analysis. The phase behaviour as related to the morphology was investigated by determining the relaxation transitions of the thermoplastic-modified polycyanates. D.m.a. was also used to measure the storage and loss moduli and the transition temperatures. The dimensions of the samples for d.m.a. tests were approximately 5.0 × 1.5 × 0.3 cm. Because of the flexure mode of deformation, the storage and loss moduli measured by the DMA-983 were the flexure E' and E'', respectively. The heating rate was 5°C min^{-1} and a fixed frequency of 1 Hz was used.

Scanning electron microscopy. The morphologies of the cured resins were examined using a scanning electron microscope (ISI mini-SEM). The thermoplastic-modified samples were fractured at ambient temperature since both components exhibited T_g values above room temperature. Samples containing liquid reactive rubber and thermoplastic were fractured at liquid nitrogen temperature (to ensure brittle failure of the rubber component) and at room temperature, respectively, for comparison. Subsequently, the fracture surfaces of the samples were coated with gold by vapour deposition using a vacuum sputterer.

Fracture toughness measurements. The fracture toughnesses of the cured, neat-resin (no carbon fibre) plaques of the polycyanate and modified polycyanates were determined using a double torsion (DT) technique. The DT technique and procedures have been reviewed in interesting articles by Frassine *et al.*[14,15]. The specimens were rectangular and measured 25.0 × 5.0 × 0.3 cm. All tests were carried out at room temperature. The crack propagation speed was set at 1–2 mm s^{-1}. The specimens were grooved (V notched) lengthwise on the centre line and supported on the two lengthwise edges with the groove facing downwards. A load was applied by pressing a twin roller on the top of the plaque sample directly on the opposite side of the groove. A crack was then initiated from one end of the groove, which served the purpose of guiding the crack propagation along a straight line. Once stationary crack growth conditions were met, the fracture energy G_{IC} could be easily determined from the raw data using the established equations in the literature[14,15].

RESULTS AND DISCUSSION

Thermodynamics and kinetics of phase separation

The cure reactions transform the originally homogeneous liquid blends into crosslinked networks of thermoplastic-incorporated polycyanates. For rubber-modified or thermoplastic-modified thermosetting systems, phase separation is influenced not only by thermodynamic factors but also by kinetics factors such as gelling/vitrification of the thermosetting components during cure[16,17]. Since the mixture during cure is a reactive system, the thermodynamics could be a function of the cure reaction. Therefore, the thermodynamic factors should be considered in order to understand the mechanism of phase separation. On the other hand, the kinetics of nucleation and growth might also influence the rate of phase separation and ultimately the phase domain structure and relative distributions of components in the phase domains. The thermodynamic factor can be expressed in terms of the Gibbs free energy[18]

$$\begin{aligned}\Delta G_{\mathrm{mix}} &= \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} \\ &= V(\delta_1-\delta_2)^2\phi_1\phi_2 + RT(\mathrm{N}_1 \ln \phi_1 + N_2 \ln \phi_2)\end{aligned} \tag{1}$$

where subscript 1 represents the polycyanate component and subscript 2 represents the thermoplastic component. ΔH_{mix} and ΔS_{mix} are the heat of mixing and entropy of mixing, respectively, T and V are the temperature and volume, and the N_i, ϕ_i, and δ_i are the numbers of segments, volume fractions, and solubility parameters, respectively.

The fact that the cyanate resin and the thermoplastic (PSu or PEI) form a homogeneous, miscible mixture before cure suggests that the solubility parameters of the thermosetting and thermoplastic components are closely matched. During the cure reaction, the thermodynamic contribution of the thermoplastic component remains constant at a constant cure temperature. However, the thermodynamic contribution of the thermosetting component does not remain constant as the cure progresses. As the cure reaction transforms the monomeric dicyanate molecules into a crosslinked polycyanate network, the polar cyanate (OCN) functional groups are converted to less polar triazine rings (*Scheme 1*). The difference between the solubility parameters increases to a finite value as the cure progresses. As a result, the enthalpic ΔH_{mix} term becomes more positive. Additionally, the cure reaction also results in an increase in the molecular weight, which reduces the entropic contribution (ΔS_{mix}). The combination of an increase in the enthalpy of mixing and a decrease in the entropy of mixing results in a more positive free energy of mixing. Phase separation occurs as a result of the free energy changing from negative or zero to a positive value.

Phase behaviour and domain structure

Figure 1 shows the d.s.c. results for the T_g values of the PSu-modified polycyanates at various compositions. Slight broadening of the T_g transition was observed for the modified polycyanates at some compositions. Other than that, the T_g values of the thermoplastic and thermosetting polycyanate phases remained constant and were absolutely independent of composition. All the PSu-modified polycyanates were cured and post-cured at exactly the same temperatures. The T_g results suggest that the PSu-modified polycyanate did develop a phase-separated morphology with complete immiscibility

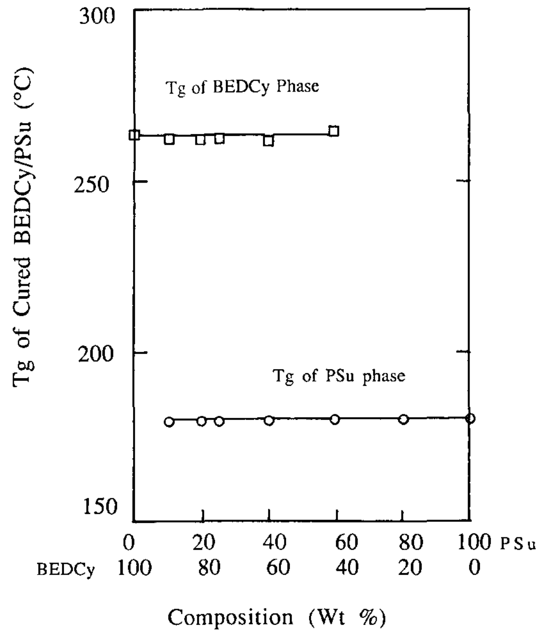

Figure 1 Plots of T_g *versus* composition for the PSu-modified polycyanates

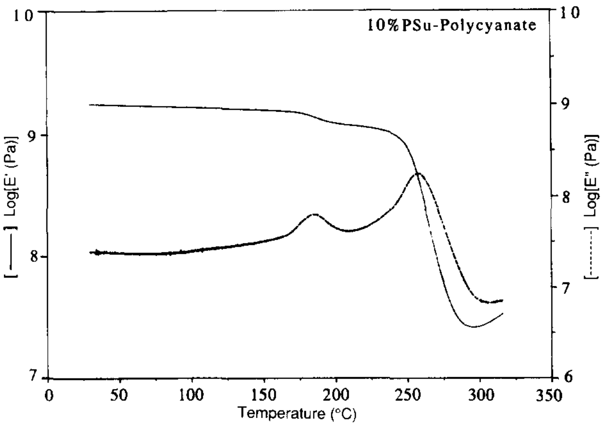

Figure 2 D.m.a. results for the 10 wt% PSu/polycyanate sample

in all compositions investigated, indicating that the thermoplastic phase was completely separated from the polycyanate phase. The phase behaviour of the PSu-modified and PEI-modified polycyanates was further inferred from the results of dynamic mechanical analysis.

The d.m.a. results for the PSu-modified polycyanates at various thermoplastic PSu contents of 10, 20, and 60 wt% are given in *Figure 2*, which shows the storage and loss moduli as a function of temperature for the 10 wt% PSu/polycyanate sample. The storage and loss modulus curves clearly exhibit two transitions at 185°C and 260°C, respectively. The lower temperature transition is smaller in magnitude and is the T_g of the PSu component. The higher temperature transition, also greater in its magnitude of relaxation, is the T_g of the polycyanate component. Apparently, the magnitudes of the transitions as measured by the peak heights are approximately in agreement with the relative compositions of the components. At the composition of 10 wt% PSu, the continuous phase of the modified network is apparently the polycyanate component. The d.m.a. results (similar to *Figure 2* but not shown here) for the 10 wt% PEI/polycyanate sample showed similar features to those for the 10 wt% PSu/polycyanate sample, except that the PEI phase exhibited a relaxation peak at 210°C. Again, at this composition the continuous phase was apparently the polycyanate component of the 10 wt% PEI/polycyanate network.

Figure 3 shows the d.m.a. results for the 20 wt% PSu/polycyanate sample. The storage and loss modulus curves clearly exhibit two transitions at about the same temperatures as the d.m.a. results for the 10 wt% PSu analogue (*Figure 2*). However, the height of the relaxation peak for the PSu component is greater than that for the polycyanate component. This result might be unusual, considering that the PSu constitutes only 20 wt%. This phenomenon is interesting and needs an explanation. The phase continuity might gradually shift from that of predominantly the thermosetting polycyanate component for the 10 wt% PSu/polycyanate sample to a co-continuity formed by both the thermoplastic and thermosetting components for the 20 wt% PSu/polycyanate network. Partial phase inversion (the continuous phase changing from thermosetting to thermoplastic) seems to have taken place at 20 wt% of PSu in the PSu-modified polycyanate. Formation of a continuous phase by the thermoplastic component at a relatively low weight fraction of 0.2 might seem interesting but unusual. Further results from the microscopic and solvent sorption studies will be presented and discussed in later sections.

Figure 4 shows the d.m.a. results for the 60 wt% PSu/polycyanate sample prepared by solution blending. Surprisingly, the storage and loss modulus curves now exhibit only one apparent transition at 185°C for the PSu phase, and the polycyanate component is identified only as a barely visible transition at a higher temperature. Apparently, the height of the relaxation peak for the PSu component (60 wt%) is disproportionately much greater than that for the polycyanate component (40 wt%). An explanation can be provided as follows. At increasing contents (20 wt% and above) of the PSu component in the PSu/polycyanate network, the continuity of the polycyanate phase domain deteriorates while the continuity of the PSu component rapidly expands and coexists with the continuous phase of the polycyanate. At even higher contents, the PSu component eventually substitutes the polycyanate component as the continuous phase. At 60 wt% of PSu in the PSu/polycyanate sample, the main continuous phase is no doubt predominantly the PSu component. As a result, the polycyanate phase, being dispersed in the continuous PSu phase, cannot support itself once the temperature is increased to beyond the T_g of the polysulfone component. The relaxation peak of the now dispersed phase domain formed by the polycyanate component therefore cannot be easily identified by d.m.a. as a result of significant softening of the continuous PSu phase.

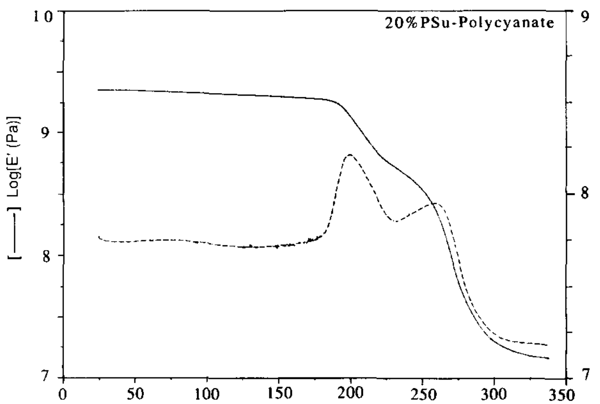

Figure 3 D.m.a. results for the 20 wt% PSu/polycyanate sample

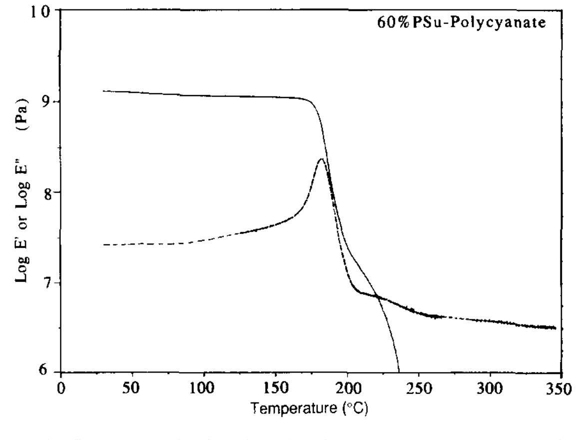

Figure 4 D.m.a. results for the 60 wt% PSu/polycyanate sample

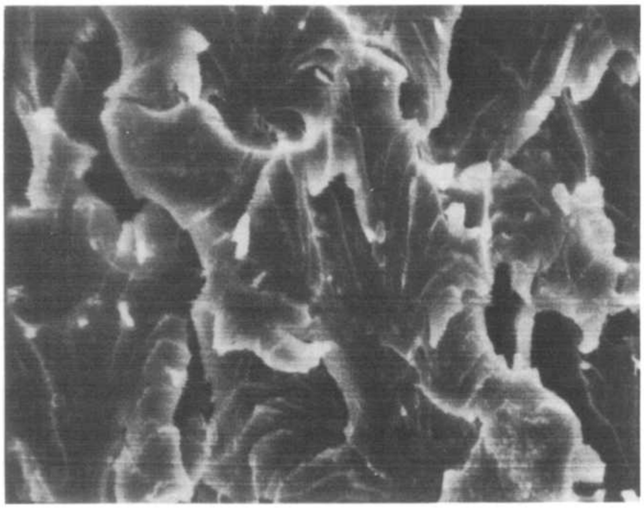

Figure 5 SEM micrograph (2000 ×) of the fracture surface of the 10 wt% PEI/polycyanate sample

Morphology

Both the d.s.c. and d.m.a. results as discussed above clearly indicate that the 10 wt% PEI/polycyanate sample forms a two-phase network. At low thermoplastic contents below 10 wt%, the morphologies of the modified polycyanates are similar to that of the neat polycyanate. *Figure 5* shows the micrograph of the 10 wt% PEI/polycyanate sample. The morphology as shown by scanning electron microscopy (SEM) at 2000 × provides a direct visualization of the phases, their degrees of mixing, and their continuities. The fracture surface of the 10 wt% PEI/polycyanate sample might look superficially like that of a neat polycyanate; however, a closer inspection of the micrograph reveals that there are some scattered particles of submicrometre size, barely visible and submerged within the shear-banded polycyanate fracture surface. These tiny particles are the thermoplastic PEI domains, phase separated from the continuous polycyanate phase domain. At this composition, the cyanate component, not the thermoplastic PEI component, forms the continuous phase in the network of the modified polycyanate. Accordingly, the microscopy results agree with the interpretation obtained from the d.m.a. results for the 10 wt% PEI/polycyanate sample.

At higher thermoplastic contents, significantly different morphologies are observed. *Figure 6* shows the SEM micrographs of the fracture surfaces of the 20 wt% PEI/polycyanate (*Figure 6a*) and 25 wt% PSu/polycyanate (*Figure 6b*) networks. Both micrographs show distinct phase separation morphologies, with heavily precipitated particles spherical or oval in shape. The major difference is in the dimensions of the particles. The average diameter of the particles in the 20 wt% PEI/polycyanate sample is about 2 μm or greater, while the average size of the particles in the 25 wt% PSu/polycyanate sample is only 0.8 μm or less. Note that some particles in the PEI/polycyanate network had been detached during the fracture treatment from the fracture surface of the sample and only craters were left prior to the SEM examination. Similar detachments occurred in the PSu/polycyanate network, except that the particles were smaller and the craters were not so easily visible.

There might seem to be some confusion over which component or components constitute the continuous phase in the modified polycyanate networks. *Figure 6a* (for the 20 wt% PEI/polycyanate network) shows that the particles are of the same nature and therefore should be of the same constituent. Do these particles consist of thermoplastic PEI? That is, does the PEI form the dispersed phase domain and the polycyanate form the continuous phase? Judging from the volume and number of the particles present in the fracture surface, the answers to the above questions should be in the negative. The total volume percentage of the PEI component is only approximately 20% in the modified polycyanate. The volume of the particles, including the craters, is apparently much greater than 20%. This analysis leads to the conclusion that the particles could only be formed as a result of precipitation of the thermosetting polycyanate component. However, not all the polycyanate component is precipitated into particles. Some portion of the polycyanate component might still remain in the continuous phase. The micrograph shows that some part of the continuous phase domain (the domain surrounding the particles) exhibits extreme ductile shear banding characteristic of the thermoplastic PEI. It seems likely that the continuous phase is simultaneously formed by two mutually immiscible PEI and polycyanate phases in a parallel mode.

In summary, as the thermoplastic content in the

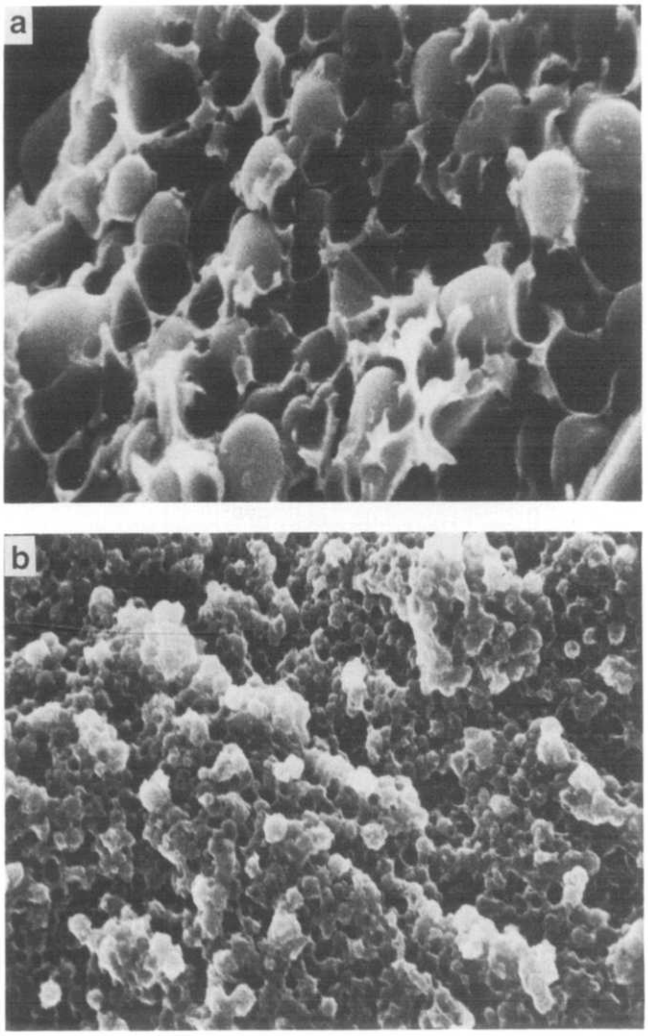

Figure 6 SEM micrographs of the fracture surfaces of (a) the 20 wt% PEI/polycyanate sample (5000 ×) and (b) the 25 wt% PSu/polycyanate sample (2500 ×)

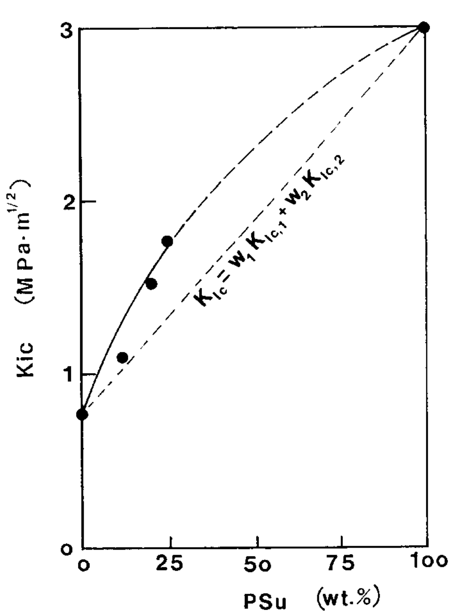

Figure 7 K_{IC} of the PSu-modified polycyanates as a function of PSu content

modified polycyanate network is increased from 10 wt% to 20 wt% and above, the thermoplastic starts to retreat from the discontinuous phase domain and participates in the continuous phase. In the meantime, while a portion of the thermosetting polycyanate remains in the continuous phase and forms a co-continuous phase together with the thermoplastic component, some of the thermosetting component begins to precipitate in the discontinuous phase by forming particles spherical or oval in shape. Eventually, at thermoplastic contents greater than 20 wt% in the modified polycyanate, the thermoplastic component is precipitated predominantly in the continuous phase domain, while the polycyanate component is precipitated in the continuous domain as well as in the discontinuous domain. This unique morphology therefore consists of a co-continuous domain formed simultaneously by the thermosetting and thermoplastic components, with the excess thermosetting component precipitating to form dispersed particles.

One might expect that the thermoplastic PEI or PSu component forming part of the continuous phase would greatly enhance the fracture toughness of the modified polycyanate. On the other hand, the solvent resistance might suffer significantly because of the co-continuity comprising thermosetting and thermoplastic components. The mechanical and physical properties will be presented and discussed in later sections. Similar co-continuous phase morphologies have also been observed for some reactive systems such as in the reaction-injection moulding (RIM) of copolymers of poly(urethane–urea) by Ryan[19], who reported that the moduli of the co-continuous copolymers yielded a good fit to the Davies equation[20].

Fracture toughnesses of modified polycyanates

Figure 7 shows a plot of the fracture intensities K_{IC} of the PSu-modified polycyanates as a function of PSu content in the cured thermoplastic/polycyanate network. The two extremes (0 wt% and 100 wt%) on the composition axis of the figure represent neat polycyanate (BEDCy) and neat polysulfone (PSu), respectively. The solid curve describes the actual trend in the experimental data for the fracture toughnesses of the PSu-modified polycyanates, while the dashed line between the two composition extremes indicates the K_{IC} of the modified networks calculated according to the well-known rule of mixtures

$$K_{IC} = \omega_1 K_{IC,1} + \omega_2 K_{IC,2} \qquad (2)$$

where subscript 1 represents the polycyanate phase and subscript 2 represents the PSu phase, and the ω_i are the volume fractions. The figure shows that there is an abrupt jump between the two data points for the K_{IC} of the 10 wt% PSu/polycyanate and 20 wt% PSu/polycyanate networks. At low PSu contents (10 wt% or lower), the K_{IC} of the PSu/BEDCy semi-IPNs show a linear relationship with the composition (PSu weight fraction). However, at PSu contents greater than 20 wt%, the curve of the fracture toughness for the PSu-modified polycyanates shows a positive deviation from the linear relationship for the K_{IC} of the PSu/polycyanate networks. The abrupt change in the K_{IC} at the thermoplastic content of 20 wt% could be attributed to the previously discussed phase inversion from a continuous thermosetting domain to a more complex morphology in which the thermoplastic PSu forms a co-continuous phase together with a continuous BEDCy phase.

The fracture toughness results also support the previous interpretation obtained from the d.m.a. and microscopy results that at thermoplastic contents greater than 20 wt% phase inversion becomes gradually evident. The fracture toughness improvement is apparently influenced by the phase morphology and continuity of the thermoplastic-modified polycyanate. The co-continuous morphology accounts for the impressive improvements in fracture toughness observed for the modified polycyanates with thermoplastic contents greater than 20 wt%. The thermoplastic/polycyanate mixtures with higher thermoplastic contents (greater than 30 wt% thermoplastic in the blend) were not suitable for mechanical testing of fracture toughness owing to the difficulty in blending large weight percentages of thermoplastic with the dicyanate, as mentioned earlier.

Interestingly, the PEI-modified polycyanate showed a toughness improvement slightly below the weight average. In a direct comparison with the analogous PSu-modified polycyanate, the fracture toughness of the 20 wt% PEI/polycyanate sample is listed in *Table 1*. In the table, the fracture intensities K_{IC} are listed along with the fracture energies G_{IC} calculated from $K_{IC}^2 = EG_{IC}/(1-\nu^2)$, where the Poisson ratio ν is taken as 0.35, and E is the modulus of the modified polycyanate. The 20 wt% PEI/polycyanate mixture exhibits a K_{IC} of 1.10 MPa m$^{1/2}$, which is significantly lower than that of the 20 wt% PSu/polycyanate mixture. Apparently, at a thermoplastic content of 20 wt%, a co-continuous morphology occurs in both the PEI-modified and PSu-modified polycyanates.

Table 1 Fracture toughnesses of modified and unmodified polycyanates

Sample	G_{IC} (J m^{-2})	K_{IC} (MPa m$^{1/2}$)
10 wt% PEI/10 wt% PSu/polycyanate	650	1.50
20 wt% PSu/polycyanate	600	1.45
20 wt% PEI/polycyanate	350	1.10
Unmodified polycyanate	160	0.80

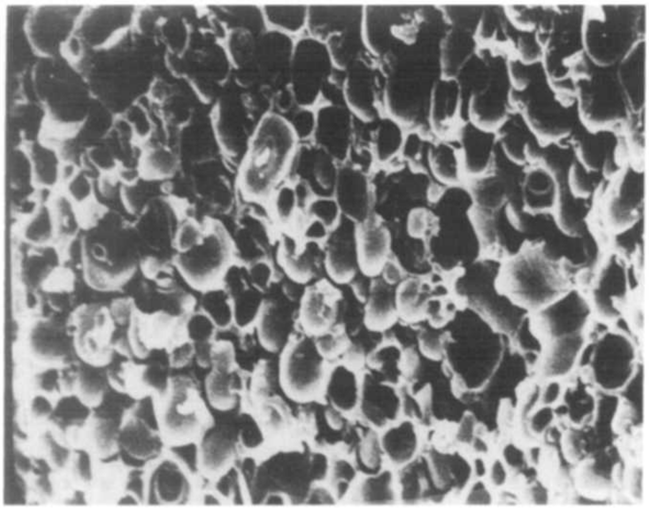

Figure 8 SEM micrograph (1500×) of the 10 wt% PEI/10 wt% PSu/polycyanate sample

However, at the same thermoplastic content, PEI is not as effective as PSu in enhancing the fracture toughness. The difference can be readily explained from the differences in particle sizes and size distributions for these two modified polycyanates at 20 wt% of PEI or PSu. As discussed earlier, the PSu-modified polycyanate has a dispersed phase of particles measuring about 0.8 μm or less. By contrast, the PEI-modified polycyanate contains particles of about 2 μm or larger. Assuming that the influence of the co-continuous morphology is the same in the PEI-modified and PSu-modified polycyanates, the particle size might be an equally critical factor. Precipitated particles with diameters larger than 1–2 μm seem to be unfavourable for improving the fracture toughness. The results suggest that in addition to phase continuity, the particle size and the size distribution also influence the fracture toughness of the modified polycyanate.

In addition, a sample was prepared where the cyanate resin was modified with equal loadings of both PEI (10 wt%) and PSu (10 wt%). The resulting cured polycyanate contained a total of 20 wt% of two different thermoplastics (PEI and PSu). *Figure 8* shows the SEM micrograph of the fracture surface of this thermoplastics-modified polycyanate sample. The micrograph reveals that particles of two average sizes are present in the 10 wt% PEI/10 wt% PSu/polycyanate mixture. The larger particles of 2–3 μm are apparently characteristic of the PEI-modified polycyanate, and the smaller particles (1 μm) are characteristic of the PSu-modified polycyanate.

Table 1 compares the fracture toughnesses of the thermoplastics-modified polycyanate and the polycyanates modified only with PSu or PEI. While the K_{IC} of the 20 wt% PEI/polycyanate mixture is only 1.10 MPa $m^{1/2}$, that of the 10 wt% PEI/10 wt% PSu/polycyanate mixture is much higher at 1.50 MPa $m^{1/2}$, which is also higher than that of the 20 wt% PSu/polycyanate mixture.

Solvent sorption behaviour

Further attempts were made to prove that the thermoplastic constitutes the co-continuous phase domain in the modified polycyanates with thermoplastic contents greater than 20 wt%. The co-continuous phase morphology could also be inferred from the results of the solvent sorption behaviour of the modified polycyanates. Since both PSu and PEI thermoplastics easily dissolve in methylene chloride, observation of the dissolved domains in the samples should reveal whether the domains were of a thermoplastic or thermosetting nature. A 25 wt% PSu/polycyanate sample was fractured and immersed in methylene chloride for approximately 1–2 min. Subsequently, it was withdrawn from the solvent and sputter coated with gold and examined by SEM.

Figure 9 shows the micrograph of the solvent-treated 25 wt% PSu/polycyanate sample. The particles have remained in the sample, giving further evidence that the particles in the dispersed phase are of a thermosetting nature. In contrast, the continuous phase domain has been significantly smeared by the solvent, indicating that the thermoplastic has been etched out of the continuous phase domain by the solvent treatment. Again, note that the presence of craters should not be mistaken as evidence of solvent etching, since most of the craters were formed during the fracture process as discussed earlier.

Figure 10 compares the methylene chloride (CH_2Cl_2) solvent sorptions of the various PSu-modified polycyanates. The results of solvent sorption show that the modified polycyanates absorb CH_2Cl_2 faster and are thus poorer in terms of solvent resistance than the unmodified BEDCy polycyanate matrix at an equivalently cured state. However, the figure shows that the changes in solvent resistance are abrupt and not continuous, as evidenced by the significant gap between the sorption curves for the 10 wt% PSu/polycyanate and 20 wt% PSu/polycyanate samples. Such abrupt changes were also similarly observed for the fracture toughnesses of the modified polycyanates. The neat polycyanate (BEDCy) with no thermoplastic incorporated in the matrix is quite resistant to aggressive solvents such as methylene chloride even after long exposure. At 10 wt% PSu loading, the modified polycyanate is similarly resistant to methylene chloride since its sorption curve is closely parallel to the sorption curve of the neat polycyanate. However, with a 20 wt% or higher content of PSu (or PEI) in the modified polycyanate, the resulting thermoplastic/dicyanate network exhibits considerably poorer solvent resistance. In methylene chloride the 20 wt% PSu/polycyanate sample quickly becomes swollen and disintegrates into crumples in the solvent in about two hours at ambient

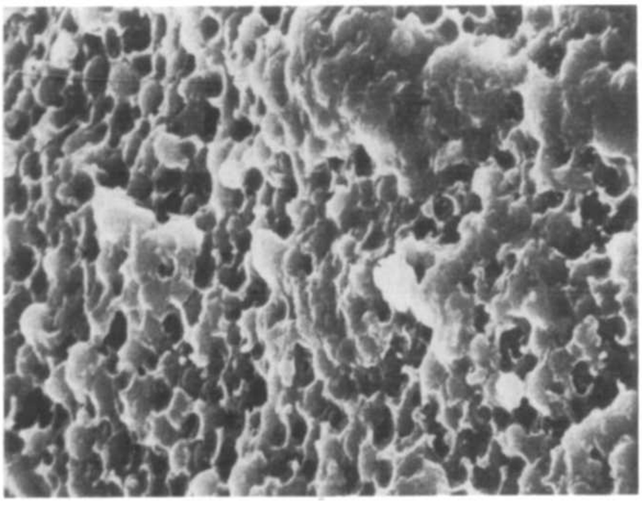

Figure 9 SEM micrograph (2500×) of the solvent-treated (methylene chloride) 25 wt% PSu/polycyanate sample

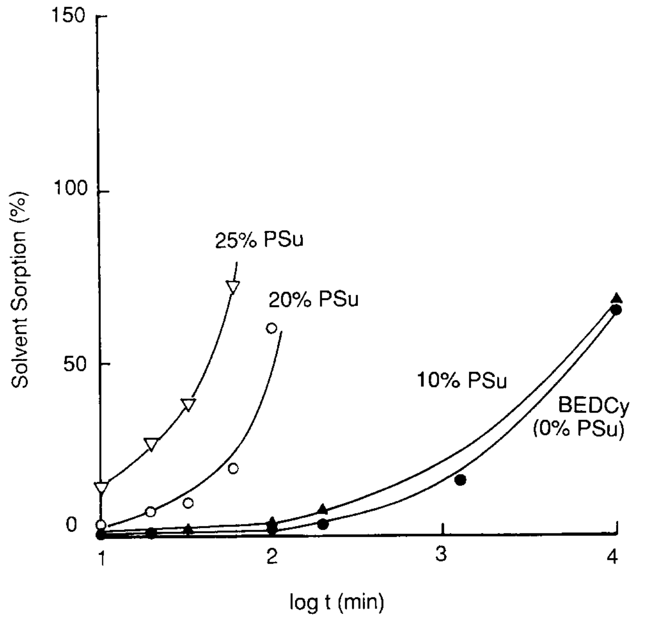

Figure 10 Methylene chloride solvent resistances of the various PSu-modified polycyanates: (●) neat polycyanate; (▲) 10 wt% PSu/polycyanate; (○) 20 wt% PSu/polycyanate; (▽) 25 wt% PSu/polycyanate

temperature. The co-continuous morphology, which contributes to a better than additivity improvement in K_{IC}, also downgrades the solvent resistance of the modified resin system.

CONCLUSIONS

The d.s.c. results indicate that, at all thermoplastic compositions, the thermoplastic-modified polycyanates form an immiscible, phase-separated heterogeneous network. The d.m.a., SEM, fracture toughness, and solvent sorption results all consistently suggest that the thermoplastic-modified polycyanates exhibit an interesting morphology with the phase continuity changing as the content of the thermoplastic in the thermoplastic/polycyanate network increases. At low thermoplastic contents between 0 and 10 wt%, the thermosetting BEDCy polycyanate component forms the continuous phase domain while the discrete domain is primarily composed of the thermoplastic (PSu) component. However, the continuous phase changes from the thermoset to the thermoplastic and thermoset when the thermoplastic content is about 20 wt% or higher. The phase inversion is quite complete for the thermoplastic component, but only partial for the thermosetting polycyanate component. As a result, the thermosetting component is found to precipitate not only in the continuous phase but also in the dispersed phase as spherical or oval particles.

The domain structures of the thermoplastic-modified polycyanates are completely different from those of elastomer-modified thermosets, where the elastomeric component usually precipitates to form rubber particles which act as energy absorbers or crack stoppers. Also, the morphologies of the thermoplastic-modified polycyanates are different from those of thermoplastic-modified epoxies, where the thermoplastic component predominantly precipitates in the dispersed phase domain.

The co-continuity of the phase domains comprising the thermoplastic and thermosetting components of the thermoplastic-modified polycyanate significantly influences the fracture toughness and solvent resistance. While the co-continuity helps to improve the fracture toughness, it also significantly downgrades the solvent resistance owing to the continuity of the thermoplastic component. In addition to the co-continuity, the sizes and size distributions of the precipitated polycyanate particles in the dispersed phase are also influential in determining the magnitude of the increase in fracture toughness in the thermoplastic-modified polycyanates.

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REFERENCES

1 Grigat, E. *et al. Kunstst. Plast.* 1968, **58** (12), 827
2 Woo, E. M., Fukai, B. and Seferis, J. C. *Proc. 3rd Tech. Conf. Am. Soc. Compos.* Seattle, 1988, p. 192
3 Shimp, D. A., Hudock, F. A. and Bobo, W. S. *Proc. 18th Int. SAMPE Tech. Conf.* Seattle, 1986, p. 851
4 Delano, C. B. and Harrison, E. S. *SAMPE Ser.* 1975, **20**, 243
5 Shimp, D. A. *SAMPE Q.* 1987, **19**, 4146
6 Arnold, C., Mackenzie, P., Malhotra, V., Pearson, D., Chow, N., Hearn, M. and Robinson, G. *Proc. 35th Int. SAMPE Symp.* Anaheim, 1990, p. 128
7 Yang, P. C., Woo, E. P., Laman, A. A., Jakubowski, J. J., Pickelman, D. M. and Hsu, H. J. *Proc. 36th Int. SAMPE Symp.* Anaheim, 1991, p. 437
8 Papathomas, K. L. and Wang, D. W. *J. Appl. Polym. Sci.* 1992, **44**, 1267
9 Bauer, M., Bauer, J. and Kuhn, G. *Acta Polym.* 1986, **37**, 715
10 Osei-Owusu, A., Martin, G. C. and Gortro, J. T. *Polym. Eng. Sci.* 1991, **31**, 1604
11 Zeng, S., Ahn, K.-J., Seferis, J. C., Kenny, J. M. and Nicolais, L. *Polym. Compos.* 1992, **13**, 191
12 Bucknall, C. B. and Gilbert, A. H. *Polymer* 1989, **30**, 213
13 Woo, E. M., Bravenec, L. D. and Seferis, J. C. *Polym. Eng. Sci.* in press
14 Frassine, R., Ricco, T., Rink, M. and Pavan, A. *J. Mater. Sci.* 1988, **23**, 4027
15 Ricco, T., Frassine, R. and Pavan, A. *J. Mater. Sci.* 1990, **25**, 1517
16 Donatelli, A. A., Sperling, L. H. and Thomas, G. A. *J. Appl. Polym. Sci.* 1977, **21**, 1189
17 Hsich, H. S.-Y. *Polym. Eng. Sci.* 1990, **30**, 493
18 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979, Ch. 2, p. 51
19 Ryan, A. J. *Polymer* 1990, **31**, 707
20 Davies, W. E. A. *J. Phys. D* 1971, **4**, 1176