Model with Experimental Evidences for the Morphology of Binary Blends of a Thermosetting Polycyanate with Thermoplastics

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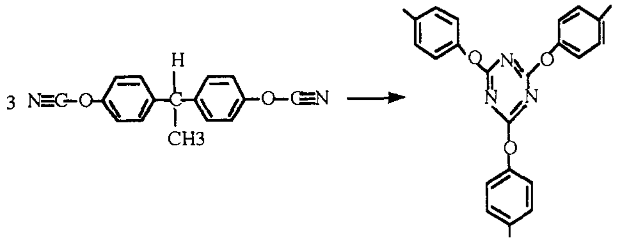
ABSTRACT: A proposed mechanical model based on our modification of the conventional Takayanagi model was successfully used to describe the dynamic mechanical modulus data of binary blends of a high-temperature thermosetting polycyanate (Bisphenol E dicyanate) with thermoplastics (polysulfone or poly(ether imide)). The model parameters were found to quantitatively agree well with the physical compositions of the phases in the blends. The modeling results suggested interesting shifts in the phase continuity of the blends as a function of the thermoplastic contents. At low thermoplastic contents (10% and below), the blends exhibited a simple continuous-dispersed phase morphology, with the continuous polycyanate phase surrounding the dispersed phase. As the thermoplastic contents increased (20 vol % and above), a notable change in the phase composition and morphology was observed in the dispersed domains, and a continuous thermoplastic phase started to form, while the polycyanate continuous phase retreated rapidly. The findings from the modeling were also further experimentally substantiated by optical and electron microscopy observations.

Introduction

Among the recent technologically important thermosetting matrix resins for advanced high-temperature composites, aromatic cyanate resins such as Bisphenol E dicyanate (BEDCy) and Bisphenol A dicyanate (BADCy) are attracting increasing interest. The chemical structure of BEDCy is



They are low-viscosity resins that can cross-link to form polycyanates by forming very thermally stable cyclic triazine rings, which resemble cyclic ester rings except that the oxygen atom is now a nitrogen atom. For that reason, dicyanates are also called cyanate ester resins. Polycyanates possess low dielectric constants and high thermal stabilities.[1] The cured dicyanates, or polycyanates, all possess high glass transition temperatures (250-280 °C), low water sorption, and excellent processability and compatibility with carbon fibers.[2] Recent studies have focused on their potential matrix applications in advanced composites.[3-10] A balance of properties can be exploited by incorporating suitable thermoplastics into dicyanate resins. Modification of the polycyanates by introducing thermoplastics into the liquid resins prior to cure has been proven to yield an impressive enhancement in fracture toughness. The toughening mechanism generally depends on a process where phase separation takes place as an originally miscible liquid mixture of the cyanate resin and thermoplastic is transformed into a cross-linked network. Control and prediction of phase morphology of the thermoplastic-modified polycyanates become quite complex. Continuity of the phase domains comprised of the thermoplastic and the thermosetting components has been found to significantly influence the fracture toughness, solvent resistance, and other properties of the thermoplastic-modified polycyanates.[11]

Mechanical modeling has been developed in the past for understanding the phase behavior, continuity, and effects of morphology on mechanical performances of polymer systems with a heterogeneous phase morphology. The Takayanagi model[12] has been utilized by a number of authors to describe the mechanical behavior of various multiphase polymer systems. Examples are found in oriented semicrystalline polymers,[13,14] blends and copolymers.[15-17] and interpenetrating polymer networks.[18] These polymer systems all exhibit a relatively simple continuous-dispersed phase morphology; i.e., one component forms the continuous phase and the other component(s) comprises the discontinuous phase, whose domains are dispersed and surrounded by the continuous phase domain.

A thermoplastic-thermoset blend usually exhibits a quite complex morphology that also changes significantly with the relative component composition in the blend. There would be difficulty for the model to be applied to polymer systems of such a complex phase morphology. By properly modifying the Takayanagi model, an analytical modeling approach was developed in this study to quantitatively describe the shift of phase continuity as the compositions of thermoplastic and dicyanate changed. The process of phase separation and formation of the domain structure of the cured thermoplastic-modified polycyanate blends are discussed. By investigating the suitability of the modified model in describing the data of dynamic mechanical properties of the blends in a wide composition range, we have attempted to determine the mode and scale of thermoplastic segregation from the

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thermoset network and to obtain a better understanding of morphological/structural effects on the properties of a multiphase thermoplastic-modified polycyanate blend system.

Experimental Section

The BEDCy dicyanate resin used was obtained from Rhone Poulenc, Inc. (U.S.A. Division). The resin was of a high-purity quality and was used as received. Two amorphous thermoplastic polymers were used to blend with the dicyanate resin. The thermoplastics were polysulfone (Amoco UDEL^R P1700) with a T_g of 185 °C and poly(ether imide) (GE Ultem 1000) with a T_g of 210 °C. They were also both used as received. The PEI has M_n = 12 000 and M_w = 30 000. A melt mixing technique was used to prepare samples of low thermoplastic contents. However, a solvent (methylene chloride) mixing technique was used to prepare dicyanate/thermoplastic mixtures containing higher thermoplastic contents (higher than 20%). A catalyst, which as supplied is a 20:1 mixture of nonylphenol with copper acetylacetonate, was used at about 2 wt % of the resin mixture. The solvent-processed mixtures were carefully degassed at low temperatures to drive out most of the residual solvent prior to cure reactions. After mixing, the resin mixtures were poured into a glass mold which had been treated with a mold release agent. Cure reactions were performed for the thermoplastic/dicyanate mixtures by heating to 177 °C with an isothermal hold for 2 h at that temperature, followed by a postcure at 220 °C for 2 h.

Dynamic mechanical analysis (DMA) was performed by using a DuPont DMA-983 in a flexural bending mode. The storage and loss moduli were recorded automatically by a DuPont TA-2000 system for data acquisition and analysis. A heating rate of 5 °C/min and a fixed frequency of 1 Hz were used. A differential scanning calorimeter (Perkin-Elmer DSC-7) was used for measuring residual heat or reactions and for observing the glass transition temperature of the blends. The morphology of the thermoplastic-modified polycyanate samples was studied by using optical and electron microscopy techniques. The samples were fractured at ambient temperatre and then placed on the sample mount of a Nikon cross-polarized optical microscope. For SEM studies, the fractured samples were first coated with gold sputtering and subsequently examined by use of a JEOL (JSM-35) scanning electron microscope.

Results and Discussion

Modeling of Continuous–Discrete Morphology. The DSC results indicated that the binary blends of the thermoplastic with dicyanate resin were miscible at all compositions before cure of the thermosetting component. However, after full cure, the clear dicyanate/thermoplastic mixtures turned into a cross-linked thermoplastic–thermoset network with a cloudy appearance. Phase heterogeneity was apparently observed for all cured thermoplastic-modified polycyanate blends of all compositions, as evidenced by the DSC and DMA results revealing two T_g's. In order to describe the morphology changes as the thermoplastic contents were varied in the polycyanate networks, simple models consisting of elements representing the continuous and disperse phases were used. Four combinations, parallel, series, parallel–series, and parallel–series–parallel models, are shown in Figure 1 (diagrams A–D). The parallel elements represent continuous phases and the series elements represent dispersed phases. In the figure, A is the thermosetting component and U is the thermoplastic component. Both A and U may be in the continuous or discontinuous phases. λ is the volume fraction of the discrete phase in the blend, and ϕ is the fraction of the thermoplastic component in the discrete phase. The product, $\phi\lambda$, is therefore the volume fraction of the U component in the discrete phase. In Figure ID, an additional parallel element representing a continuous U phase is added, and ξ is the volume fraction of U in that new phase.

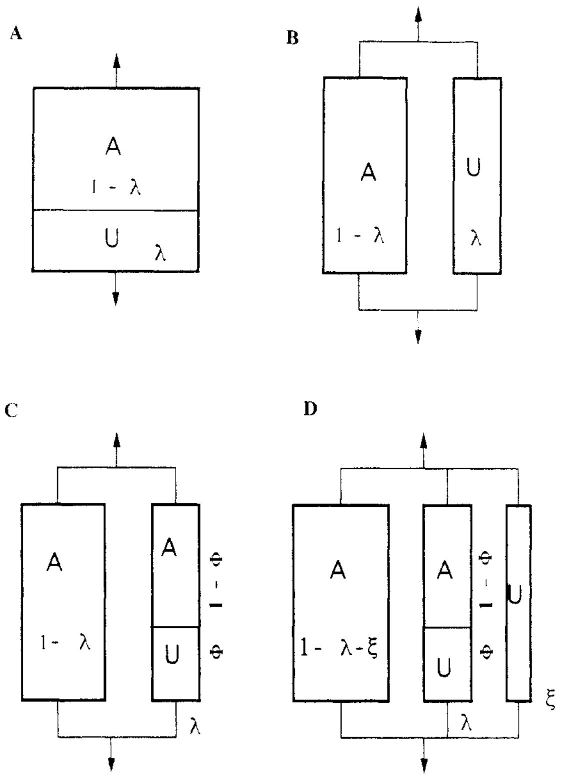

Figure 1. Series (S), parallel (P), parallel–series (P–S), and parallel–series–parallel (P–S–P) models.

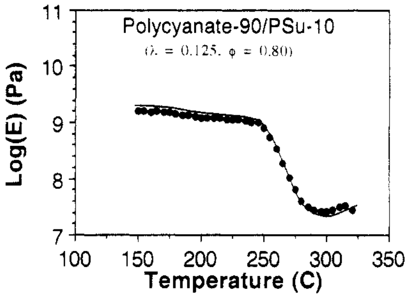

Figure 2. log modulus vs temperature for the 90:10 polycyanate/PSu blend. The experimental data are compared with the prediction according to the Takayanagi model with λ = 0.125 and ϕ = 0.80.

At relatively low thermoplastic (TP) contents (10% and below) in the polycyanate network, there was no doubt that the polycyanate component formed the only continuous phase, while the thermoplastic component was dispersed in the continuous phase. The DMA and microscopic results suggested that most of the thermosetting polycyanate component formed the major continuous phase, while a small fraction of the polycyanate component was precipiated along with the thermoplastic component, which together formed the minor dispersed phase. To quantitatively describe the component distribution in these two phases, a mechanical model was fitted with the storage modulus data. Figure 2 shows a comparison between the experimental storage modulus data of the 90:10 polycyanate/polysulfone blend with the calculated values according to the Takayanagi model,[12] which is in fact a combination of both the parallel and series models and shown in Figure 1C:

$$E = (1-\lambda)E_A + \lambda/[(1-\phi)/E_A + \phi/E_U] \tag{1}$$

where λ is the volume fraction of the discontinuous phase consisting of both components A and U, $1 - \lambda$ is the volume fraction of the continuous phase, and ϕ is the volume fraction of the thermoplastic (U) component in the discontinuous phase. A good fit to this model infers a simple continuous–dispersed morphology for the blend, and the parameters obtained from the model may be used to determine the relative compositions in the phases. The best fitting was obtained with parameters $\lambda = 0.125$ and $\phi = 0.80$. The values of the parameters for the 90:10 polycyanate/polysulfone blend suggest that the polycyanate component forms the only continuous phase domain, which accounts for 87.5 vol % of the blend, and that the remaining 12.5 vol % is occupied by the dispersed phase domain consisting of primarily the thermoplastic polysulfone (80 vol % of the dispersed phase) and a much smaller fraction of the polycyanate component (20%).

Formation of an Additional Continuous Phase. The DMA and microscopy data suggested that, as the thermoplastic (TP) contents were increased beyond 10 vol % in the blends, the dispersed phase domain gradually increased in size while the thermosetting polycyanate continuous phase domain began to recede. In addition, the thermoplastic component also gradually formed another continuous phase that coexisted with the retreating polycyanate continuous phase. At this time, the polycyanate was not the only dominant continuous phase in the PSu/polycyanate blend any more. For the 80:20 polycyanate/polysulfone blend, the Takayanagi equation was found to be no longer valid for describing this now quite complex morphology and its effect on the mechanical properties of the blends required a completely different approach of interpretation. A new model was employed to describe the complex morphology that might include dual continuous phases, with a dispersed phase consisting of changing compositions of the thermoplastic and thermosetting components. This was done by properly taking into account that a certain volume fraction of the thermoplastic component was excluded from the dispersed phase and formed another continuous phase, which constituted a dual continuity along with the original thermosetting polycyanate continuous phase (A). Equation 1 is modified by adding a parallel element (E_U) and a parameter ξ to the Takayanagi model to represent the modulus and volume fraction, respectively, of this new continuous phase:

$$E = (1 - \lambda - \xi)E_A + \lambda/[(1 - \phi)/E_A + \phi/E_U] + \xi E_U \quad (2)$$

where ξ is the volume fraction of the thermoplastic (U) component that forms a co-continuous phase domain along with the continuous thermoset phae domain (A). This new model is schematically shown in Figure 1D.

Figure 3 shows the experimental storage modulus data of the 80:20 polycyanate/polysulfone blend in comparison with the calculated values according to the new model as discussed above. The best fitted model parameters for this blend are summarized in Table 1. The comparison as shown in the figure clearly tells that, within the 100–275 °C temperature range, the agreement between the theoretical and experimental data is quite impressive. The minor discrepancy at the higher-temperature side is due to experimental errors at higher temperatures caused by loosening of the specimen gripping. The parameters for the 80:20 polycyanate/polysulfone blend suggest that the polycyanate still forms the continuous phase domain but is now diminished and accounts for only $1 - \phi - \xi = 0.60$ volume fraction of the blend. The remainder of the blend is occupied by a new TP continuous phase domian (0.10 volume fraction of the blend) and an expanding dispersed TP–TS phase domain (0.30 volume fraction of the blend). It is interesting that the thermoplastic should start to form a subsidiary continuous phase when it constitutes only 20 vol % of the blend. A phase-in-phase morphology is shown to be common in most thermoplastic-modified epoxy systems,[19] but the morphology for thermoplastic–dicyanate blends seems dramatically different. Furthermore, in contrast with the dispersed phase domain of the 90:10 polycyanate/polysulfone blend where the dispersed phase is of primarily thermoplastic nature, the dispersed phase domain of the 80:20 polycyanate/polysulfone blend now consists of as reduced composition of the thermoplastic polysulfone (33 vol %) and a larger fraction of the polycyanate component (67%).

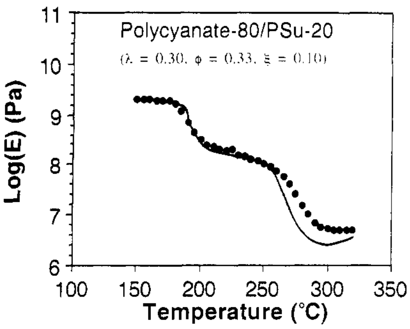

Figure 3. log modulus vs temperature for the 80:20 polycyanate/PSu blend. The experimental data are compared with the calculated values according to ther P–S–P model with $\lambda = 0.30$, $\phi = 0.33$, and $\xi = 0.10$.

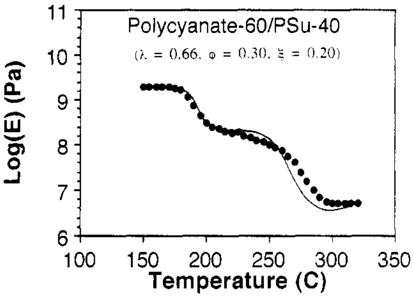

Figure 4. log modulus vs temperature for the 60:40 polycyanate/PSu blend. The experimental values are compared with the prediction according to the P–S–P model with $\lambda = 0.66$, $\phi = 0.30$, and $\xi = 0.20$.

Table 1. Modeling Parameters for Polysulfone/Polycyanate Blends with Various Polysulfone Volume Fractions

Psu, wt %	λ	ϕ	ξ	$\phi\lambda + \xi$
	Parallel–Series Model			
10	0.125	0.80	none	0.10
	Parallel–Series–Parallel Model			
20	0.30	0.33	0.10	0.199
40	0.66	0.30	0.20	0.398

Further Shift of Phase Continuity. At an even higher thermoplastic content in the binary blend, the DMA results revealed an interesting feature of the phase continuity. The DMA storage modulus data suggested that, although the thermosetting component was still the major component, the sample seemed to quickly soften disproportionally even at temperatures below the T_g of the thermosetting component. Evidently, this would not have happened had all the thermosetting polycyanate component comprised the continuous phase in the blend. Figure 4 shows the experimental storage modulus data of the 60:40 polycyanate/polysulfone blend in comparison with the calculated values according to the P–S–P model as discussed above. The agreement between the theoretical

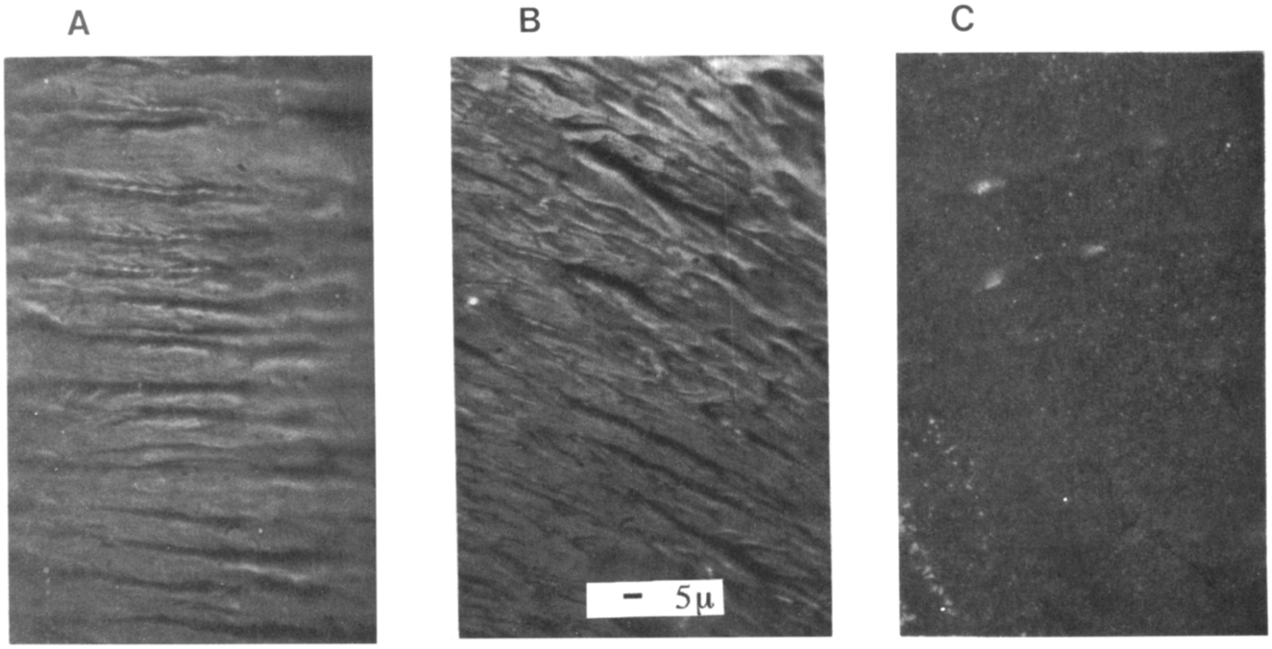

Figure 5. Optical micrographs of polycyanate/polysulfone blends: (A) polycyanate; (B) 90:10 polycyanate/PSu; (C) 80:20 polycyanate/PSu.

and experimental data is again quite impressive. The minor discrepancy at higher temperatures after the glass transition region is again attributed to experimental errors. For the 60:40 polycyanate/polysulfone blend, the best fitted model parameters (listed in Table 1) suggest that the continuous polycyanate phase domain is now greatly diminished and has an even lower presence in the blend with only $1 - \phi - \xi = 0.14$ volume fraction, although the thermosetting polycyanate component still accounts for 60 vol % of the blend. The remainder of the blend is occupied by a larger TP continuous phase domain (0.20 volume fraction of the blend) and a dramatically increasing dispersed phase domain (0.66 volume fraction of the blend). The relative composition of the thermoplastic vs thermosetting components in the dispersed phase domain stays about the same as that of the 80:20 polycyanate/polysulfone blend, i.e., consisting of the thermoplastic polysulfone (33 vol %) and the polycyanate component (67%).

Model Parameters and Phase Compositions. As discussed, the model findings have been shown to agree well with the experimental DMA results. The shift of phase continuity has been clearly observed by fitting the storage modulus data with the P–S–P mechanical model. In addition, the model parameters also accurately reflect the component compositions of the phases in the blends. For the blend with 10% thermoplastic PSu, the product of the two model parameters gave the volume fraction of the thermoplastic as $\lambda\phi = 0.10$, which agreed excellently with the actual physical composition of the PSu in the blend. For the blend with 20% thermoplastic PSu, the total volume fraction of the thermoplastic component in the blend is indicated by $\lambda\phi + \xi = 0.199$, which is exactly the physical composition of the blend. The total volume fraction of the thermoplastic component in the blend is indicated by $\lambda\phi + \xi = 0.398$, which again agrees well with the actual composition of the 60:40 polycyanate/polysulfone blend examined. Note that the two constituent components in the blends have comparable densities; thus, volume fractions are about equal to weight fractions.

Experimental Observation on the Morphology of Blends. To further clarify unambiguously the phase continuity shift in the blends, microscopic examination was performed. The typical optical micrographs of the fracture surfaces of the blneds are shown in Figure 5. The unmodified polycyanate sample clearly demonstrates a smooth fracture surface, other than some shear bands (Figure 5A). The 90:10 polycyanate/polysulfone blend (Figure 5B) exhibits a predominantly continuous phase formed by the polycyanate component, and the dispersed phase domains are only barely observable due to their quite small domain sizes. These optical findings were further substantiated by using the electron microscopy results, where a larger magnification was used. At thermoplastic contents equal to or greater than 20%, the morphology of the blend exhibited a dramatic change, as demonstrated by micrograph C of Figure 5, which shows that the 80:20 polycyanate/polysulfone blend has an increased discrete domain and the continuous phase is no longer easily observable.

We conducted electron microscopy examination to provide further clarification. The SEM results of the polycyanate/PSu blends and polycyanate/poly(ether imide) blends were found to be quite similar and closely comparable. The only difference was that the precipitated polycyanate particles in the dispersed phase domain were larger and easily observable. The SEM results of the polycyanate/poly(ether imide) are shown in Figure 6. Micrograph A (at 5000×) shows the morphology of the blend of polycyanate with 10% poly(ether imide). Clearly, the polycyanate component is the major continuous phase surrounding scattered discrete particles, which were determined to be of thermoplastic nature. Micrograph B (at 1100×) shows the fracture surface of the blend containing a total of 20% thermoplastics (10% polysulfone + 10% poly(ether imide)). At this thermoplastic content, the polycyanate continuous phase (the darker but smooth regions) is diminished and exists in isolated domains when viewed from the fractured surface, while the thermoplastic continuous phase starts to appear, which is seen in the micrograph as white, fluffy craters. In addition, the dispersed phase domains (the particles–craters region) are seen to significantly expand and include precipitated polycyanate particles of ellipsoidal shapes in these domains. The microscopy evidences are consistent with the

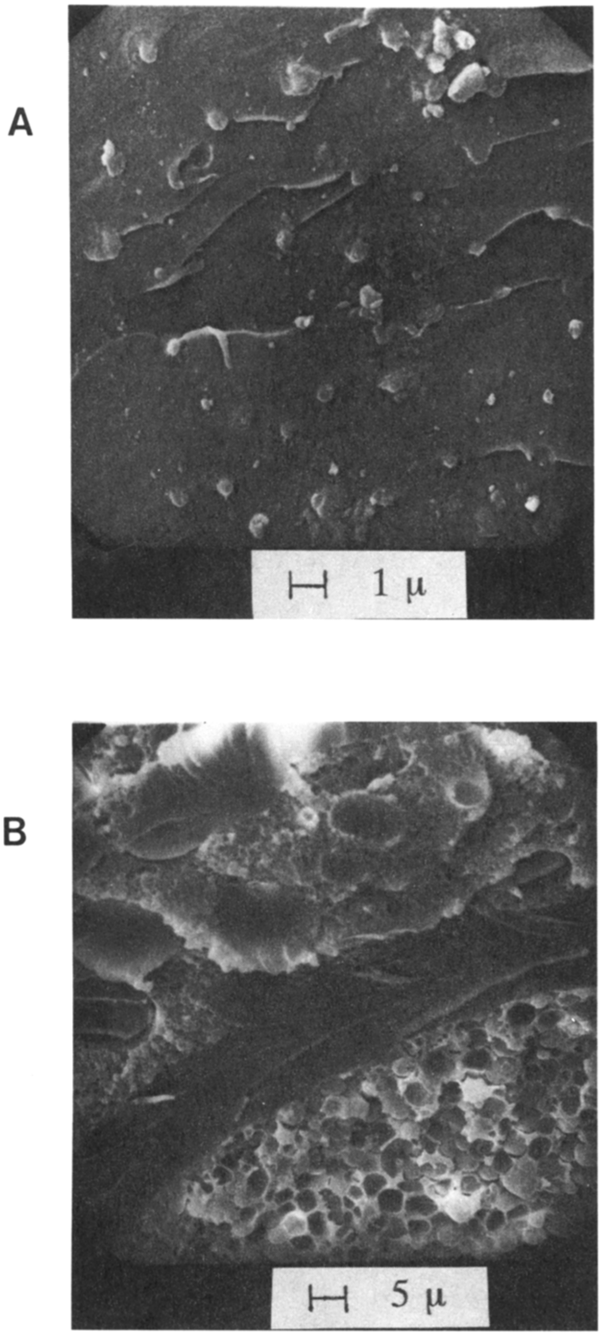

Figure 6. SEM results showing the phase transition from a simple continuous–discrete morphology to a complex dual continuity–discrete morphology: (A) blend with PEI-10; (B) blend with PSu-10/PEI-10.

findings from the mechanical modeling results.

In addition, we reported in an earlier study[11] on the solvent sorption behavior of PSu-modified polycyanate blends as a function of PSu loading in the blends that a significant gap of sorption behavior was found to exist as the PSu content was increased from 10% to 20% and above in the blends. This confirms our above findings that the continuity of the phases in the blends starts to shift at this composition from a continuous thermosetting phase to dual continuous phases formed by both the thermosetting and thermoplastic components.

Sperling et al.[20,21] have reported straight co-continuous phase or continuous–dispersed morphology for many interpenetrating networks (IPN's), which yielded good fits with the Donatelli equation,[20] or Bauer equation.[15] In addition, reacting systems such as reaction–injection molding copolymers of poly(urethane–urea) were also reported by Ryan,[22] who concluded that the modulus of the co-continuous copolymers yielded a good fit to the Davies equation.[23] Most thermoplastic polymer blends of two comparable viscosities usually exhibit a continuous–dispersed morphology.[24] A bicontinuous morphology may form, as reported for the blend of poly(phenylene oxide) and poly(styrene-co-acrylonitrile) using triblock copolymers as compatibilizers.[25,26] A "raspberry" type morphology formed as small rubber islands was reported to have an influential effect on mechanical properties.

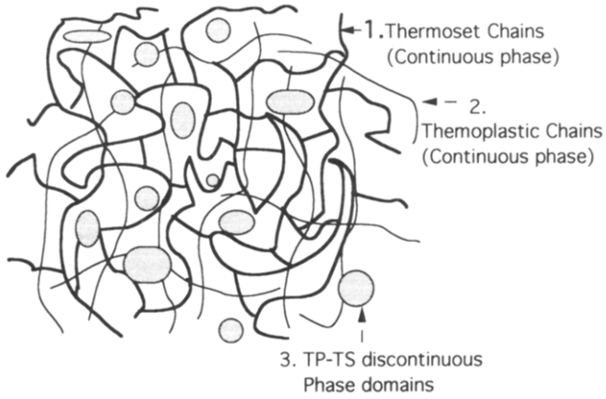

Figure 7. Simplified representation of the continuous TS–continuous TP–discrete TP–TS morphology.

It should be noted here that the morphology of the binary thermosetting/thermoplastic blends was consistently reproducible. Cure kinetics of the dicyanate resins are well studied.[3,4,6,7] Hence, cure progression for the binary blends could be easily controlled in consistent patterns. These blends are different from thermoplastic blends in that the thermosetting component is reacting and changing from a low-viscosity liquid to a highly cross-linked network. A complex continuous–dispersed–continuous morphology was developed even though there were only two components in the blends. The observation of this new morphology and its effect on mechanical properties have been attempted through a modeling approach and direct microscopic examinations. To offer a simplified view with graphical representation of this continuous–dispersed–continuous morphology, a suggested model is sketched in Figure 7. This model depicts not only dual continuous phase domains formed by the thermoplastic and thermosetting components, respectively, but also irregular, discrete domains formed jointly by coprecipitation of the thermoplastic and thermosetting components.

Conclusions

The binary blends of the thermosetting BEDCy polycyanate with the thermoplastic(s), such as polysulfone or poly(ether imide), exhibited an interesting phase-separated morphology, whose continuity and phase compositions were dependent on compositions. A new parallel–series–parallel mechanical model constructed by adding an additional parallel element to the Takayanagi model was applied to quantitatively fit with the modulus data of the bindary blends. The phase continuity, its shift, and compositional changes in the phases of the blends were then inferred from the results of the mechanical modeling. Specifically, the blends at low thermoplastic contents (10 wt % or lower) exhibited a relatively simple continuous–dispersed morphology, which could be easily described with the conventional Takayanagi model. For blends of low thermoplastic contents, the dispersed phase was primarily, though not entirely, thermoplastic, while the only continuous phase was comprised of the thermosetting polycyanate component. We discovered, however, that the morphology became significantly complicated as the thermoplastic contents were increased further, and a continuous thermoplastic phase started to appear in the blends even when the thermoplastic component was only 20% of the volume in the blend. In addition, as the thermoplastic contents were increased in the blends, the dispersed phase was found to undergo a change in the component compositions from that of primarily thermoplastic to that of a thermoset-precipitated dispersed domain. The model parameters yielded from the best fitting have been found to correlate well with the actual compositions of the phases in the blends. Furthermore, the morphology and phase structures as revealed by the modeling approach have been also experimentally substantiated by optical/electron microscopy observations.

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