

# Dicyanate Ester–Polyetherimide Semi-Interpenetrating Polymer Networks. II. Effects of Morphology on the Fracture Toughness and Mechanical Properties

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**ABSTRACT:** A high temperature thermosetting bisphenol-A dicyanate (BADCy) was modified with polyetherimide (PEI) at various compositions. The effects of the morphology of the blends on the fracture toughness and mechanical properties were investigated. For this purpose, fracture, flexural, and compression tests were carried out. The fracture surfaces of the broken specimens were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The morphology was controlled by changing the curing conditions and PEI content. A good correlation between fracture properties and microstructural features of the mixtures has been observed. The phase-inverted morphologies showed the highest fracture toughness, which was further increased by increasing the cure temperature. The mechanical properties of the matrix (modulus, yield strength) were not affected by the addition of the thermoplastic. Fracture energy values show similar trends for the different mechanical tests performed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2759–2767, 2001

**Key words:** cyanate esters; polyetherimide; morphology; toughness; mechanical properties

## INTRODUCTION

Cyanate ester resins are increasingly finding use in electronic and aerospace applications because of their excellent thermal and electrical properties.<sup>1–3</sup> However, as seen with other high performance matrices, cyanate esters exhibit relatively

brittle behavior and therefore require toughness modifications for some applications.

Toughening of these matrices can be achieved by rubber incorporation, but at the expense of high temperature performance and mechanical properties.<sup>4</sup> The toughening of highly crosslinked networks with thermoplastics has emerged as a convenient alternative to rubber toughening, particularly when high values of elastic moduli and glass transition temperature are required.

Phase separation during cure of the thermoset/thermoplastic blends is regarded as being essential to generate the toughened thermosets.<sup>5</sup> The degree of toughening is closely related to the degree of phase separation and the generated mor-

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phologies.<sup>5–9</sup> Two main factors control final morphology of the blends: thermodynamics and the kinetics of phase separation during curing. Both can be modified by changing the thermoplastic content in the mixture and/or varying the cure conditions.

In this study, semi-interpenetrating polymer networks (semi-IPNs) have been synthesized based on a high temperature thermosetting dicyanate ester and a thermoplastic, polyetherimide (PEI). In a previous work, we studied the effects of cure temperature and PEI content on the chemorheology of curing as well as on the morphology and on the related thermal properties of the dicyanate ester semi-IPNs cured by using a blend of nonylphenol and copper (II) acetylacetonate as catalyst.<sup>10</sup> The aim of this work is to study the effects of the generated morphologies on the fracture and mechanical properties of these semi-IPNs.

## MATERIALS AND METHODS

The dicyanate ester used in this study was a bisphenol-A dicyanate (BADCy) with the trade name AroCy B10, 99.5% purity, and with a cyanate equivalent of 139 g/eq. The selected thermoplastic was a commercial grade PEI (Ultem 1000) from General Electric ( $M_n = 12,000$ ;  $M_w = 30,000$ ).<sup>11</sup> The catalyst system used was a mixture of 1.78 wt % of copper (II) acetylacetonate [ $\text{Cu}(\text{AcAc})_2$ ] in nonylphenol (NP) both from Aldrich. We have previously reported that this amount of catalyst gives a high reaction rate that minimizes losses of the monomer during curing.<sup>12</sup>

Modified cyanate resins containing 0–20 wt % PEI were prepared. The mixing procedure has been reported elsewhere.<sup>10</sup> The mixtures were precured for 3 h at three different temperatures, 140, 160, and 180°C, and then postcured 2 h at 200°C, and 1 h at 250°C.

The fracture surfaces of the semi-IPNs were investigated by scanning electron microscopy, SEM Jeol JSM 35 CF, after being coated with a fine gold layer. The morphology of unfractured specimens was also studied. After being polished, samples were etched with sulfuric acid.

Atomic force microscopy (AFM) examinations of the fracture surfaces were performed in contact mode using a NanoScope IIIa of Digital Instruments. The microscope was equipped with a J Multimode SFM scanner ( $125 \times 125 \mu\text{m}$ ). Scans were performed with silicon nitride NanoProbes

with a nominal force constant of 0.06 N/m (Nanotips, Digital Instruments). The scan rate selected was 1 Hz.

For fracture testing, single-edge notched specimens (SEN) were employed. A “V” notch was cut in the sample with a rotating cutter, and a starter crack was initiated with a razor blade. Tests were performed in a three point bending mode, following the ASTM-E399 standard specification with a Instron Universal Testing Machine, Model 4206. Each reported value is the average of at least five measurements.

Flexural and compression properties were determined following the ASTM-D790 and ASTM-D695 standard specifications, respectively. At least five specimens were tested for every data point.

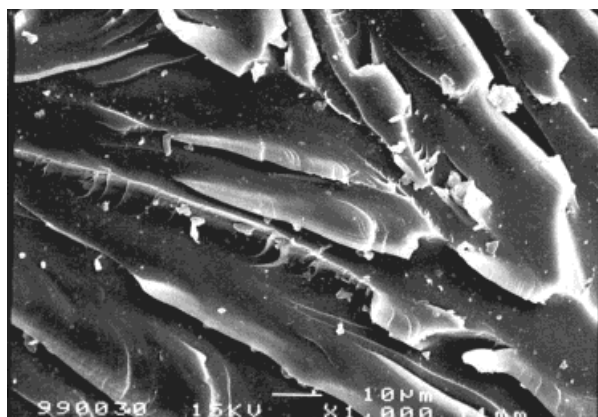
## RESULTS AND DISCUSSION

### Microstructural Analysis

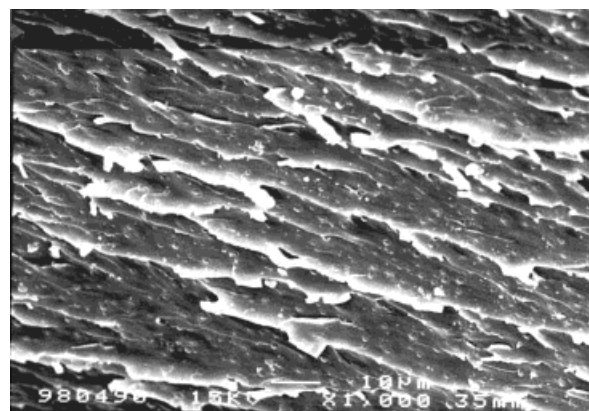
Figure 1a shows the SEM micrograph of the fracture surface of the neat BADCy matrix. The unmodified resin shows a flat and featureless surface typical of a brittle fracture. As shown below, the morphological features of the PEI-modified cyanate matrices are a function of both thermoplastic amount and cure conditions, in accordance with that reported by other authors for these matrices modified with similar thermoplastics.<sup>13–15</sup>

The fracture surface of the 5 wt % PEI blend [Fig.1(b)] looks superficially like that of neat BADCy. However, a closer inspection reveals some scattered spherical particles of PEI dispersed in the BADCy matrix, showing some signs of crack path deflection.

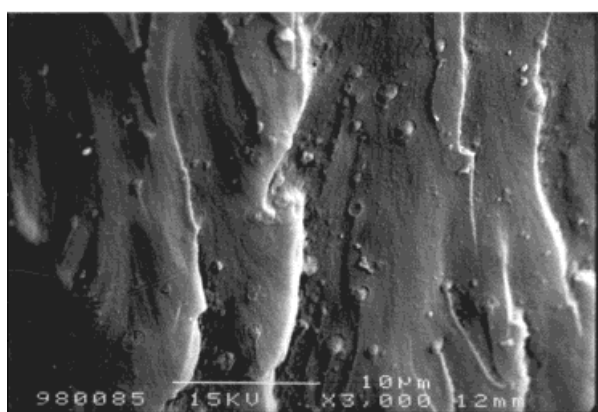
Figures 2(a) and (b) show the micrographs of the 10 wt % PEI modified BADCy precured at 140 and 180°C, respectively. The morphology is similar to that of the 5 wt % PEI blend, with PEI spheres dispersed in the BADCy matrix. The particle size distribution is not uniform—at least two particle sizes are observed. The bimodal distribution of particle sizes is usually preferred to the unimodal distribution because it produces a higher increase in the fracture toughness.<sup>16</sup> Path deflection lines are present, and some bridging between particles can be observed. There is a very small portion of particles debonded. Although PEI has no end groups to react with the cyanate and there are no chemical links between the two phases, a good adhesion between the PEI parti-



(a)



(a)

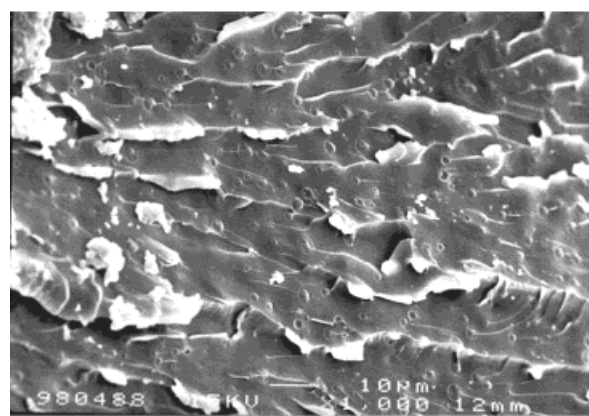


(b)

**Figure 1** (a) Fracture surface ( $\times 1000$ ) of the neat BADCy matrix. (b) Fracture surface ( $\times 3000$ ) of the 5 wt % PEI containing mixture prepared at 140°C.

cles and the matrix seems to exist. The increase of the cure temperature did not change the overall morphology of the blends but the size of the spheres increased. This behavior was attributed to a spinodal phase separation mechanism.<sup>10</sup> Although not shown, there was also a slight increase in the particle size for the 5 wt % PEI blend with the cure temperature.

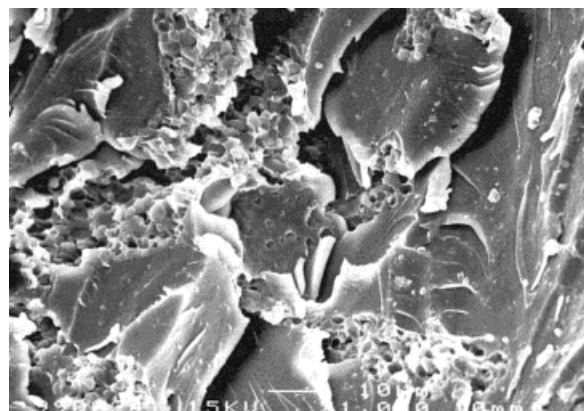
The 15 wt % PEI blend (Fig. 3) shows a morphology consisting in irregular-shape large domains. A combined structure with two co-continuous phases is observed: the cyanate-rich phase and the PEI-rich phase. There are nodules of cyanate dispersed in the PEI continuous phase showing that phase inversion had occurred in this phase. This composition is close to the critical point found in the cloud point curve (CPC) for the unreacted system (12 wt %).<sup>10</sup> This dual phase morphology is believed to be formed by a second-



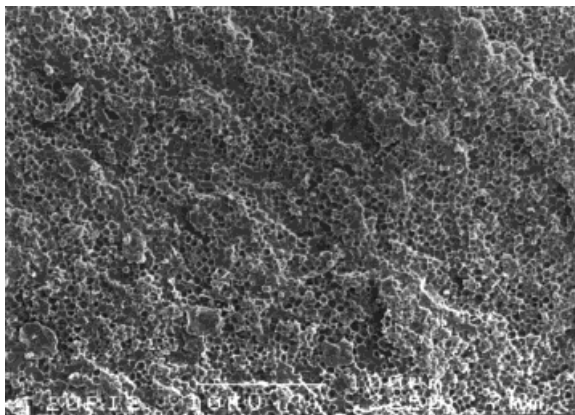
(b)

**Figure 2** Fracture surfaces ( $\times 1000$ ) of the 10 wt % PEI containing mixtures prepared at (a) 140 and (b) 180°C.

ary phase separation in the already phase-separated domains formed by the initial spinodal decomposition.<sup>17</sup> The generated morphologies were



**Figure 3** Fracture surface ( $\times 1000$ ) of the 15 wt % PEI containing mixture prepared at 140°C.



**Figure 4** Fracture surface ( $\times 250$ ) of the 20 wt % PEI containing mixture pre-cured at 140°C.

very similar at the three pre-cure temperatures. At that composition, the phase separation mechanism did not seem to be altered in the temperature range studied. In the PEI-rich phase, the matrix shows more roughness and most of the particles are debonded, meaning that the adhesion is poor. However, as for the 5 and 10 wt % PEI blends, in the BADCy-rich phase a good adhesion of the PEI particles is observed. The same behavior was reported by Oyanguren et al.<sup>18</sup> with an epoxy matrix modified with a polysulfone with nonreactive end groups. They observed regions of poor and good adhesion between the particles and the matrix depending on the nature of the continuous and dispersed phases. They associated this behavior to a higher contraction of the thermosetting-rich phase with respect to that containing the thermoplastic.

Figure 4 shows the fracture surface of the 20 wt % PEI blend pre-cured at 140°C. There appears a complete phase inversion. The PEI-phase forms the matrix and the BADCy phase appears as nodules of irregular shape. There seems to be a broad distribution of particle sizes. The fracture surface shows a very rough texture. The matrix shows ductile deformation and whereas some of the particles seem to be debonded; others seem to be broken. Observing the fracture surface, it seems that the particles were broken in the zones where the globules were bigger or more interconnected. A closer inspection was made to confirm that behavior. In order to obtain a reproducibility of the results, several areas of each sample were scanned. Figures 5(a)–(d) compares the surfaces of the unfractured and fractured specimens for the 20 wt % PEI blends pre-cured at 140 and 180°C. The unfractured specimens were observed

after removing the PEI to study which was the shape of the nodules. When the thermoplastic forms the matrix, the etching with methylene chloride is difficult. The sample quickly becomes swollen and disintegrates into crumbles.<sup>19</sup> Thus, the specimens were treated with sulfuric acid. The neat polycyanurate (BADCy) is highly resistant to the sulfuric acid, so only the PEI was removed. Figures 5(a) and (b) show the micrographs of the 20 wt % PEI mixtures pre-cured at 140 and 180°C, respectively. As can be seen, the PEI has been removed and BADCy particles remain in the sample. The mixture pre-cured at 140°C shows globules of irregular size and shape. At 180°C, the average particle size distribution seems to be higher. Figures 5(c) and (d) show the fracture surfaces of these samples. As can be seen, the biggest particles are broken. An AFM microscope was also used to have a high magnification and also to obtain a tridimensional representation of the fracture surfaces. Figures 6(a) and (b) show the fracture surface of the 180°C pre-cured blend. Cracks inside some of the particles can be appreciated and there are signs of ductile deformation of the thermoplastic surrounding them. Consequently, these experimental insights give evidence of a complex fracture mechanism for this mixture.

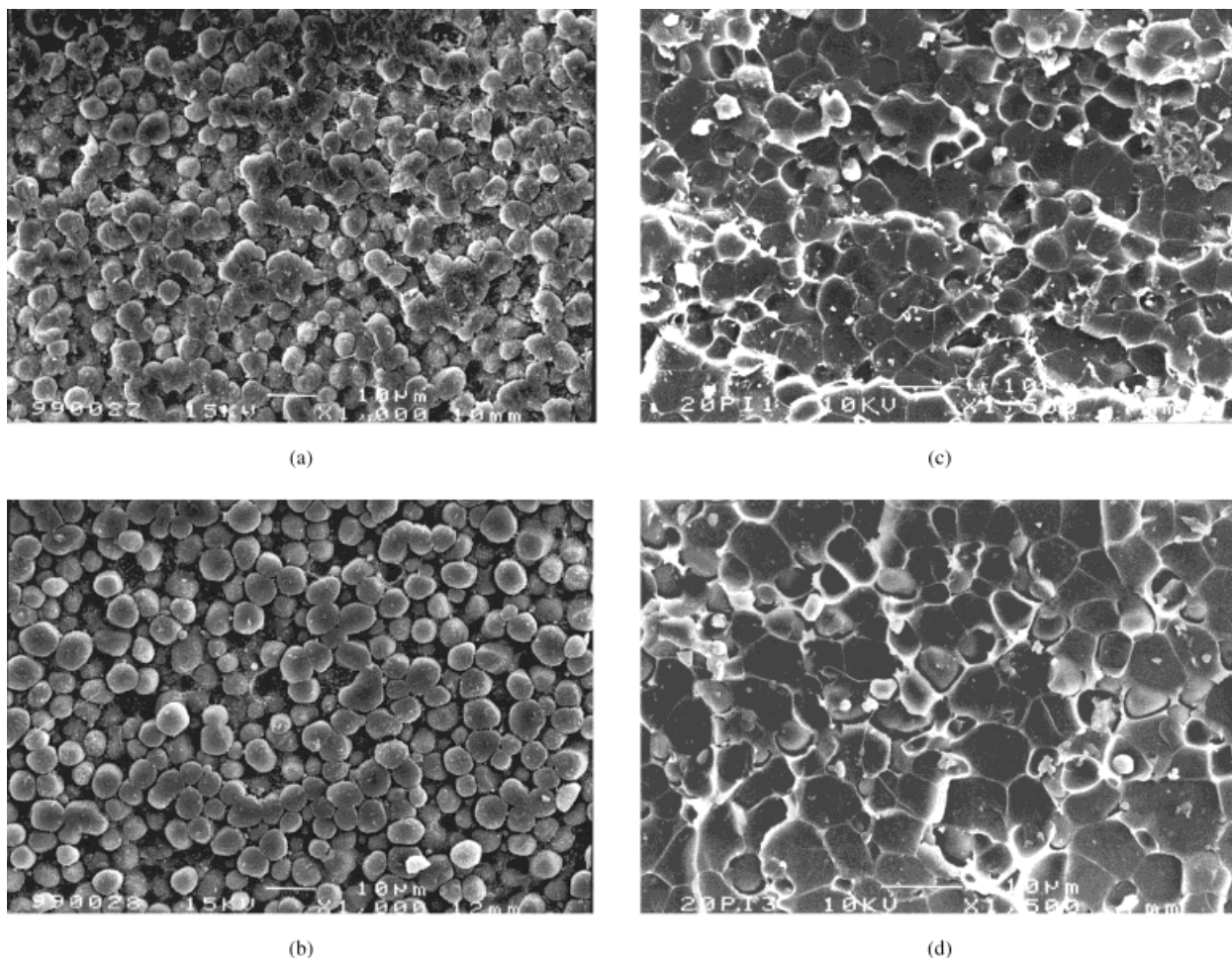
### Fracture Toughness

Figures 7(a)–(b) show the stress intensity factor  $K_{IC}$  and the fracture energy  $G_{IC}$  of the BADCy/PEI mixtures pre-cured at different temperatures as a function of the PEI content. The solid line indicates the  $K_{IC}$  calculated according to the rule of mixtures<sup>11</sup>:

$$K_{IC} = \phi_{\text{BADCy}} \cdot K_{IC\text{BADCy}} + \phi_{\text{PEI}} \cdot K_{IC\text{PEI}}$$

where  $\phi_{\text{BADCy}}$  and  $\phi_{\text{PEI}}$  represent the volume fractions of BADCy and PEI, respectively. The  $K_{IC}$  of the PEI,  $K_{IC\text{PEI}}$ , was taken as 3.61 Mpa m<sup>1/2</sup>.<sup>20</sup>

For the mixtures with 5 wt % PEI content, there was only a small increase in the fracture toughness with respect to that for the neat BADCy matrix. For the three cure temperatures, the values were only slightly higher than those predicted by the rule of mixtures. It seems that this amount of thermoplastic is not enough to produce an effective improvement of the toughness. At 10 wt % PEI loadings, a higher improvement was observed, being both  $K_{IC}$  and  $G_{IC}$  at least two times higher than those for the unmod-



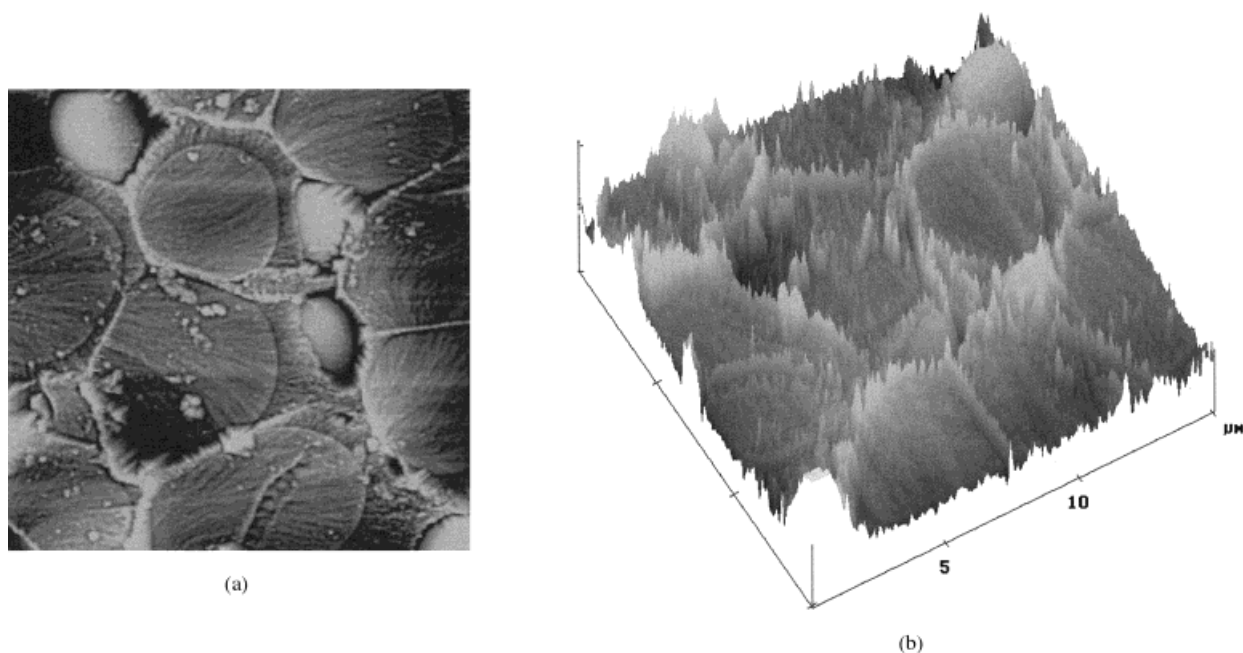
**Figure 5** Micrographs of the 20% PEI containing mixtures. Unfractured surfaces ( $\times 1000$ ) for (a) 140 and (b) 180°C precured blends. Fracture surfaces ( $\times 1500$ ) for (c) 140 and (d) 180°C precured blends.

ified matrix. The bimodal distribution observed by SEM seems to be effective. This toughness improvement was associated with the bridging and path deflection behavior present in the fracture surfaces, together with the low degree of debonding, which increased the energy required for the fracture. Such improvement with only 10 wt % PEI content is very interesting because the BADCy resin remained the matrix and the  $T_g$  of the mixture was very close to that for the neat resin.<sup>10</sup> Moreover, the solvent resistance for this kind of microstructures is much higher than in the case of the phase inverted morphologies.<sup>19</sup>

Although the effect of the temperature was masked between the experimental error, whereas there seems to be an increase in the toughness for the 5 wt % PEI mixture with increasing the cure temperature, the contrary effect was observed for

the 10 wt % PEI mixture, the fracture toughness slightly decreased with the precure temperature. In the case of low thermoplastic (TP) loadings, 5 wt %, where the particle amount and size is very small, a slight increase in the size of the particles could produce a toughness improvement. However, when the number and the size of the particles is higher, as in the case of the 10 wt % PEI blend, a higher amount of particles with lower size seems to be more effective.

The 15 wt % PEI containing mixture did not show an evident improvement of fracture toughness with respect to the 10 wt % PEI one. Whereas deformation of the PEI-rich phase was observed (Fig. 3), the amount of phase inversion did not seem to be enough to produce a high improvement of the toughness. They were no significant variations upon precure temperature.



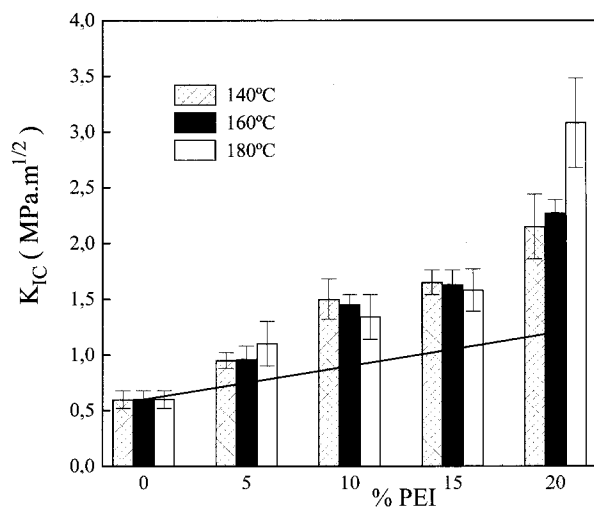
**Figure 6** AFM images (a) two-dimensional and (b) three-dimensional (15  $\mu\text{m}$  magnification) of the 20 wt % PEI containing mixtures prepared at 180°C.

In the case of the 20 wt % PEI containing mixtures, where phase inversion had occurred, there was a high increase in the fracture toughness that was exceptionally high in the case of the 180°C prepared mixture. The increase of fracture toughness in the case of phase-inverted morphologies is usually associated to the ductile deformation of the thermoplastic matrix.<sup>19,20</sup> The  $K_{IC}$  and  $G_{IC}$  calculated values were higher than those reported in the literature for modified cyanate matrices.<sup>19,21–24</sup> We have not found any reference of the BADCy resin modified with PEI, cured at similar conditions, or with the same catalyst. Lee et al.<sup>25</sup> reported that the Izod impact strength of the uncatalyzed BADCy matrix increased from  $\approx 20$  to  $\approx 40 \text{ kJ m}^{-2}$  when it was modified with 20 wt % of PEI but they did not report any  $K_{IC}$  value. Moreover, the BADCy/PEI mixtures seemed to have a different phase separation behavior when they were catalyzed<sup>10</sup> due probably to the higher polymerization rate. Wo et al.<sup>19</sup> modified a BEDCy cyanate resin with 20 wt % PEI and reported a  $K_{IC}$  value of only  $1.10 \text{ MPa m}^{1/2}$ . They stated that the average size of the nodules, which was about  $2 \mu\text{m}$  or greater, was unfavorable for improving fracture toughness. However, they found that a mixture of both 10 wt % PEI and 10 wt % polysulfone, which showed large particles of PEI and smaller particles of polysulfone, had a  $K_{IC}$  much

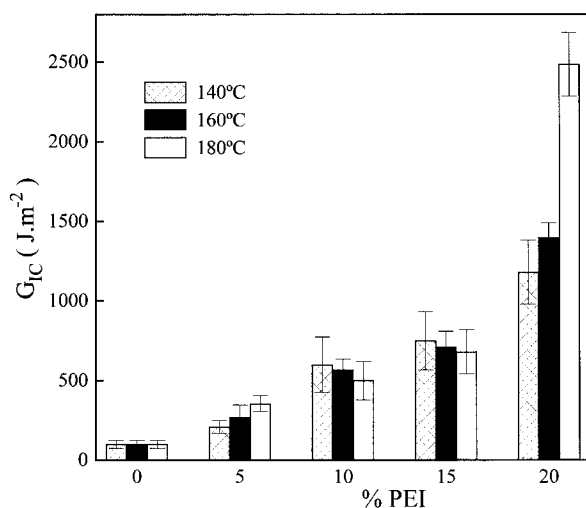
higher ( $1.5 \text{ MPa m}^{1/2}$ ), being also higher than that for the 20 wt % polysulfone blend. So, a bimodal distribution of particle sizes was found to be much more effective to enhance fracture toughness. On the other hand, Cho et al.<sup>20</sup> founded that in the case of a TGDDM/PEI epoxy matrix with a phase-inverted structure, the  $K_{IC}$  value increased from 1.01 to  $1.60 \text{ MPa m}^{1/2}$  when the size of the particles was increased from  $0.5\text{--}1 \mu\text{m}$  (nonspherical particles) to  $8\text{--}10 \mu\text{m}$  (spherical particles) by increasing the cure temperature. Thus, the fracture toughness of these kinds of morphologies seems to be highly influenced by the shape, particle size and size distribution of the particles. So, the high fracture toughness of the 20 wt % PEI containing matrix prepared at 180°C should be related to its morphological features. As shown in Figure 5(b), the 180°C prepared mixture showed bimodal size distribution with small spherical particles and big globules. The globules were bigger than in the mixtures cured at lower temperatures [Fig. 5(a)]. That morphology could lead to a higher amount of thermoplastic between the particles, making the crack path go more easily through the PEI matrix, and producing a higher plastic deformation.

### Mechanical Properties

Figures 8(a)–(c) show the flexural modulus, yield strength and strain to break of the BADCy/PEI



(a)



(b)

**Figure 7** Stress intensity factor (a) and fracture energy (b) of the BADCy/PEI mixtures precured at 140, 160, and 180°C.

mixtures precured at 140, 160, and 180°C as a function of the PEI content. The samples showed a relatively brittle behavior, fracture happening very close to yield point for the mixtures with PEI contents lower than 15 wt %. As can be seen in Figure 8(a), there were not significant changes in the flexural modulus of the BADCy when PEI was added. This could be attributed to the fact that the modulus of the neat PEI ( $3126 \pm 63$ )<sup>19</sup> is very close to that of the BADCy ( $3330 \pm 70$ ). There were no significant changes in the flexural strength [Fig. 8(b)], taking into account the experimental error. Therefore, the modification with PEI has the additional advantage that the me-

chanical properties of the neat BADCy matrix are maintained at similar performances. There was an evident increase of the strain to fracture for the 20 wt % PEI mixture [Fig. 8(c)], this increase being higher for the blend precured at 180°C. These results are in agreement with fracture test results. Again, more energy was necessary to break the specimens.

Due to the relatively brittle nature of the samples, compression tests were also carried out in order to have more information about fracture behavior. Figures 9(a) and (b) show the strength and strain at yield and to break for samples precured at 160°C as a function of PEI content. In compression tests, the samples showed a much more ductile behavior being the yield strength and strain far away from the breaking point. As happens in flexural tests, no significant changes were found in the compression modulus ( $2700 \pm 50$ ), or yield strength ( $150 \pm 9$ ), with the addition of the thermoplastic. However, there was an increase in the strength and strain to break in the case of the phase-inverted morphologies, in agreement with the fracture toughness tests.

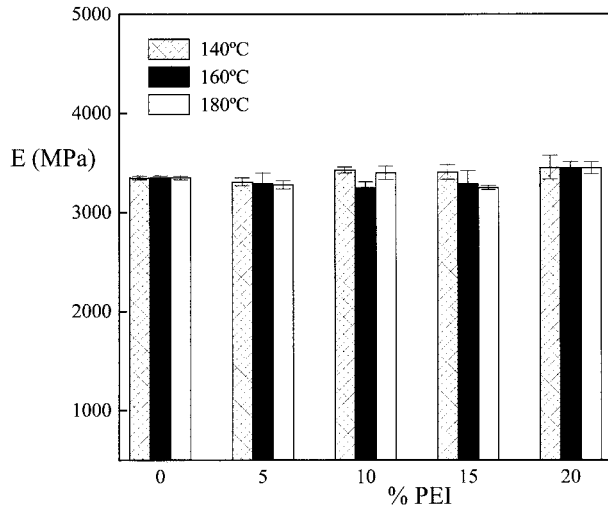
## CONCLUSIONS

A high temperature thermosetting bisphenol-A dicyanate, BADCy, was modified with PEI at various compositions. The toughness of the BADCy/PEI blends was closely related to their final morphology, which was controlled by changing the curing conditions and PEI content.

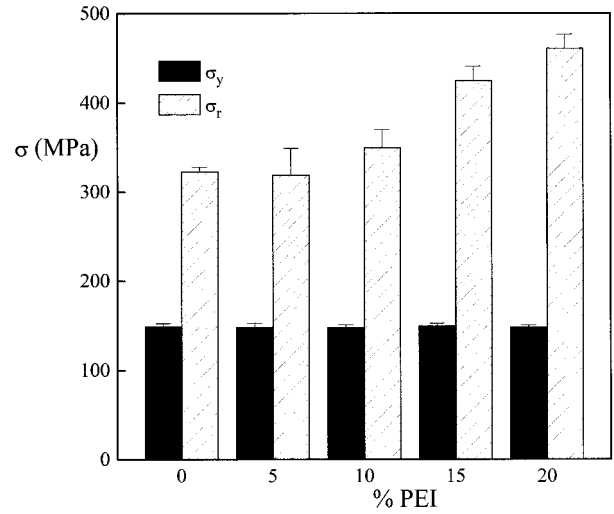
There was an increase in the fracture toughness with respect of the neat matrix in all the composition range studied (0–20 wt %). With only 10 wt % PEI loadings, where the structure was formed by PEI spheres dispersed in the BADCy matrix, both  $K_{IC}$  and  $G_{IC}$  were at least two times higher than those for the unmodified matrix. For the 15 wt % PEI blends, which showed dual phase morphologies, the toughness improvement remained similar to those for the 10 wt % ones. It was necessary to have a complete phase inversion, at PEI contents higher than 15 wt %, to have a sharp increase of the fracture toughness.

For the phase-inverted morphologies, the toughness was further improved by increasing the cyanate particle size and broadening the distance between the cyanate particles at high cure temperatures.

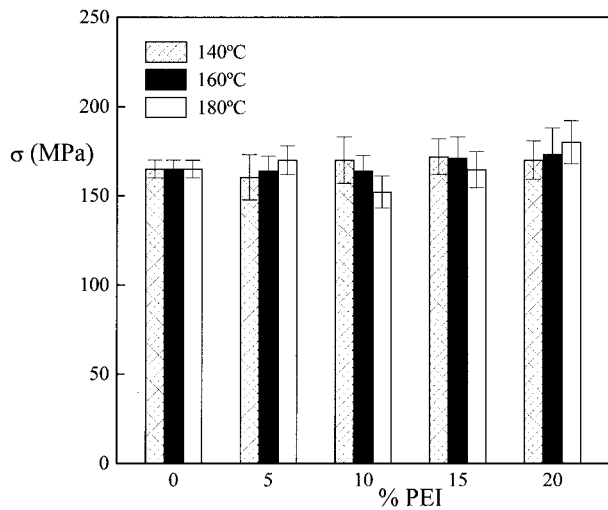
The low strain mechanical properties of the cyanate matrix (modulus, yield strength) were



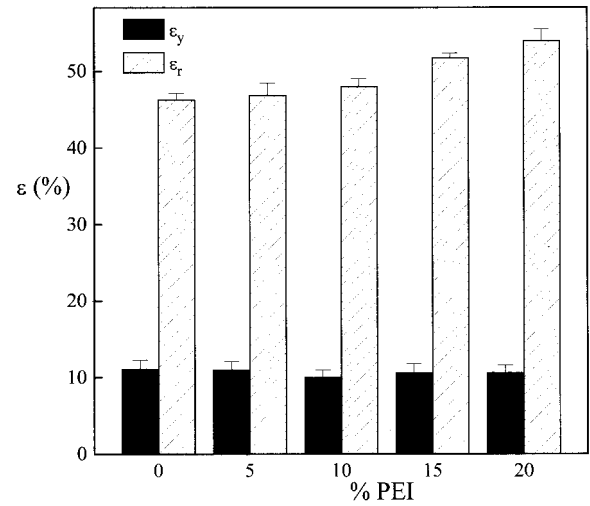
(a)



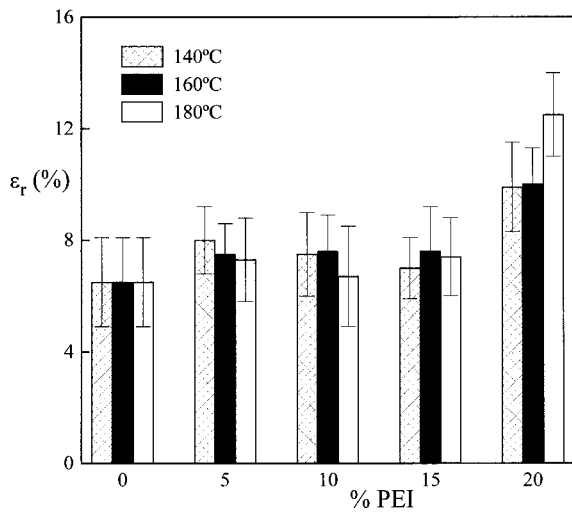
(a)



(b)



(b)



(c)

**Figure 9** Compression properties of the BADCy/PEI mixtures prepared at 160°C. (a) Yield strength and strength to break and (b) yield strain and strain to break.

not affected by the addition of the thermoplastic. The increase in strain to break was evident for flexural but also for compression testing. This increase in the deformability conducted to higher values of strength to break in compression tests.

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**Figure 8** Flexural properties of the BADCy/PEI mixtures prepared at 140, 160, and 180°C. (a) Modulus, (b) yield strength, and (c) strain to break.



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