

Morphology and Fracture Properties Relationship of Epoxy-Diamine Systems Simultaneously Modified With Polysulfone and Poly(ether imide)

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An epoxy-diamine system was simultaneously modified with two immiscible thermoplastic polymers, polysulfone (PSF) and poly(ether imide) (PEI), to develop tough materials without adding high quantities of modifiers, in order to avoid the processibility problems caused by the high initial viscosity of the mixtures. The mechanical behavior of blends containing 10 and 15 wt% total thermoplastic was analyzed and compared with the generated morphologies. The scanning electron micrographs (SEM) of the broken surfaces showed that when a small part of PEI is replaced by PSF, drastic changes in morphology, leading to co-continuity between the phases, occurred together with fracture (critical stress intensity factor, K_{IC}) improvements. As an additional advantage, no noticeable decrease in the elastic modulus (E) of final materials was observed. POLYM. ENG. SCI., 45: 1312-1318, 2005. © 2005 Society of Plastics Engineers

INTRODUCTION

The two methods used to enhance the macroscopic toughness of thermoset polymers are: 1) plasticization and 2) the increase in the number of toughening mechanisms by the generation of a heterogeneous structure.

The first method is based on the incorporation of a low glass transition temperature (T_g) component, soluble in the thermoset polymer. In this case, the increase in the fracture toughness is achieved, causing a decrease in T_g and in yield stress. For these reasons, this is not a technique that is typically used.

In the second case, the most frequently used methods to enhance toughness are the addition of particles, or the in situ formation of rubber or thermoplastic (TP) particles dispersed in the thermoset matrix. The principal limitation of using a rubbery modifier is the fact that, as in the

case of a soluble component, the improvement takes place at expenses of a decrease in other desirable properties. Then, the toughening induced by modification with TP was an alternative explored during the last decade [1–3] that allowed obtaining a tough material without a decrease in T_g or stiffness. The toughening induced by adding a TP is closely related to diverse structural factors, such as volume fraction and morphology of the dispersed phase [4].

The simultaneous modification of the thermosetting precursors with two TP polymers is an alternative to obtain different properties, according to the diverse morphologies generated due to different phase behavior of the blends [5–7].

Generally, the epoxy-amine systems modified with only one TP show toughness improvements when more than 15 wt% modifier is added. In these cases the high T_g of the TP leads to high viscosity reactive mixtures that are, in consequence, difficult to process.

In this work the simultaneous modification of an epoxy-diamine (DA) system with two immiscible TPs was studied as a possibility of developing toughened materials without incorporating high quantities of modifiers that otherwise may lead to blends with high initial viscosity and therefore poor processibility.

EXPERIMENTAL

Materials

The selected monomers were a diglycidyl ether of bisphenol-A (DGEBA) epoxy (DER 332, Dow Chemicals, number-average molecular mass, M_n , equal to 349 g/mol and a hydroxyl/epoxy ratio of 0.015) and two aromatic diamines 4,4'-diaminodiphenyl sulfone (DDS, HT 976 Ciba-Geigy) and 4,4'-methylenbis(3-chloro-2,6-diethyl aniline) (MCDEA, Lonza). They were cured in a stoichiometric epoxy/amine equivalents relationship. The TPs used were polysulfone (PSF, Udel P1700, Amoco

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Contract grant sponsors: ANPCyT; CONICET; University of Mar del Plata; Fundación Antorchas (Argentina).
DOI 10.1002/pen.20407
Published online in Wiley InterScience (www.interscience.wiley.com).
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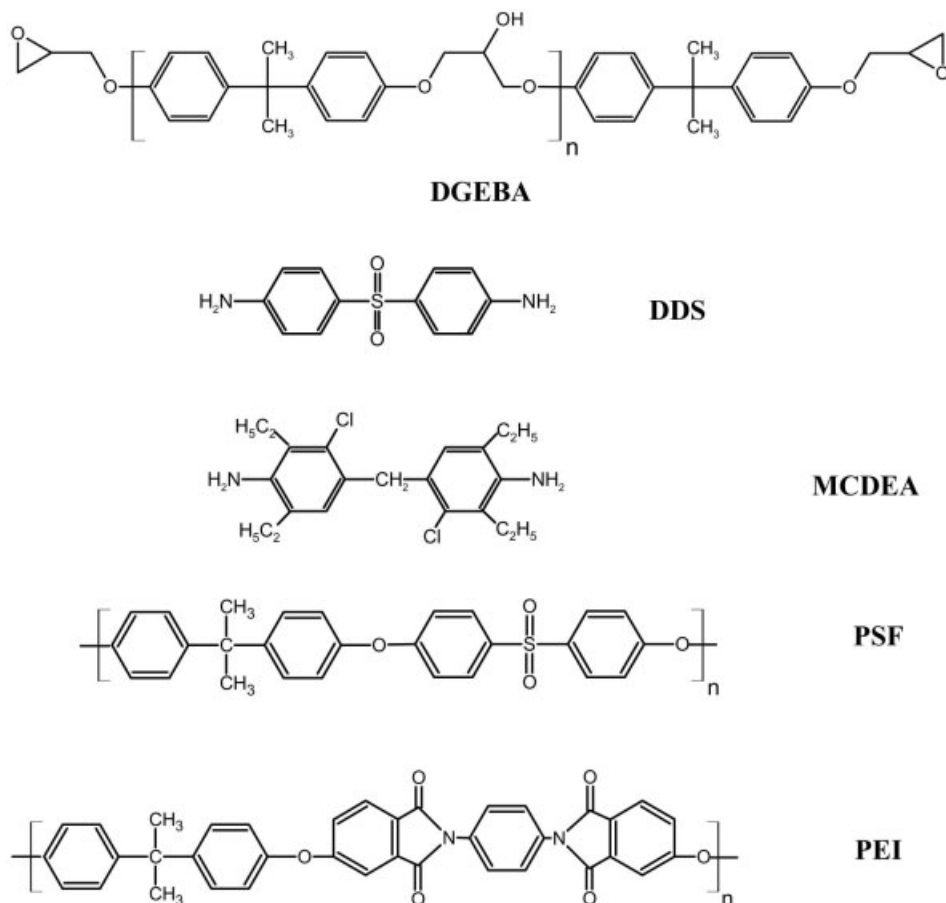


FIG. 1. Chemical structures of the epoxy monomer (DGEBA), the amines (DDS, MCDEA), and the TPs (PEI and PSF).

Chemicals, $M_n = 38,000$ g/mol, $M_w = 63,000$ g/mol) and poly(ether imide) (PEI, ULTEM 1000, General Electric, $M_n = 26,000$ g/mol, $M_w = 50,000$ g/mol). Their chemical structures are shown in Fig. 1.

Samples Preparation

Modified epoxy resins containing 0–15 wt% TP were prepared using the following procedure. The TP were dissolved in methylene chloride (CH_2Cl_2) and mixed with the resin. Most of the solvent was evaporated at room temperature and then the samples were heated to 80°C and kept at this temperature during 24 h under vacuum to eliminate the residual amount of solvent. The solution was heated (at 135°C for DDS and 90°C for MCDEA) and the diamine was dissolved by stirring for about 5 min. Air bubbles introduced during this process were removed, keeping the sample under vacuum at 150°C for 10 min. The mixtures were immediately poured into molds to prepare the specimens to be used in the mechanical characterization.

Thick plates were obtained by casting the mixture into molds consisting of two rectangular glass plaques cov-

ered by a thin Teflon[®] layer, spaced by a Teflon[®] spacer and held together with clamps. The mixture was poured into the mold that was previously heated to 200°C and

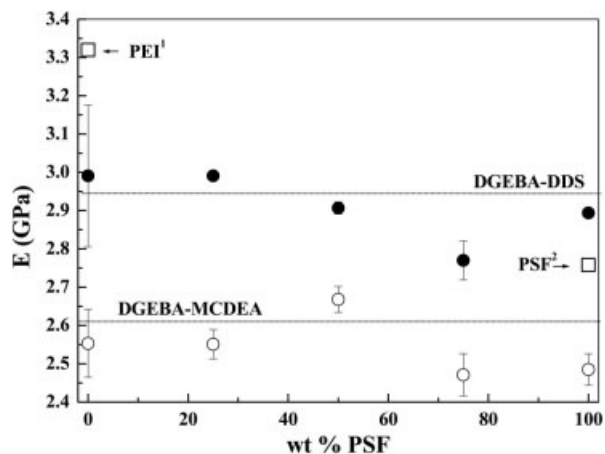


FIG. 2. Elastic modulus (E) as a function of the relative fraction of PSF, for 10 wt% PSF/PEI modified DGEBA-DA systems: (●) DDS; (○) MCDEA; (□) PEI, PSF (obtained from ¹General Electric catalog; ²Polymer Handbook, 1999 Oxford University Press [17]); (dotted lined) neat system.

$$E = S^3m/4BW^3 \quad (1)$$

where B is the thickness, W is the width, S is the support span, and m is the slope of the initial straight-line portion of the load-deflection curve.

Single-edge notched (SENB) fracture specimens were also cut from plates 5.5 mm thick using a diamond saw. Sharp notches were obtained by tapping a fresh razor blade into a machined slot so as to grow a natural crack of $0.45 < a/W < 0.55$, where a is the total crack length and W is the width of the specimen. The span-to-width (S/W) and the thickness-to-width (B/W) ratios were kept equal to 4 and 0.5, respectively.

Fracture tests were also performed in three-point bending. The critical stress intensity factor at the onset of crack growth, K_{IC} , was calculated in accordance with the ASTM D5045-91 standard [9], as:

$$K_{IC} = (P_Q/BW^{1/2})f(x) \quad (2)$$

$$f(x) = 6x^{1/2}[1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)] / (1 + 2x)(1 - x)^{3/2} \quad (3)$$

where P_Q is the critical fracture load as determined in the ASTM standard, and $x = a/W$. The total crack length a was measured from the fracture surface using a profile projector ($10\times$).

All mechanical tests were carried out in an INSTRON dynamometer 4467 at a crosshead speed of 2 mm/min, at room temperature. A minimum of five specimens were tested and average values were reported along with their deviations.

Scanning Electron Microscopy (SEM)

Fracture surfaces of TP modified SENB samples were examined by SEM, after coating the broken surfaces with a thin gold layer, using a Jeol JXA-8600 microscope.

RESULTS AND DISCUSSION

Figure 2 shows the flexural modulus values obtained for DGEBA-DA/PSF/PEI blends, containing 10 wt% total TP in different PSF/PEI proportions, as a function of PSF contribution to the total TP concentration, along with the corresponding value to the neat system (dotted line), cured at 200°C and postcured at 220°C.

It can be seen from the graph that modulus values are higher when DDS is used as hardener than in the case of MCDEA. This behavior can be explained taking into account the effect of the lower number of stable conformations afforded by the $-SO_2$ group than the $-CH_2$ group [10], which leads to higher T_g and modulus values as a

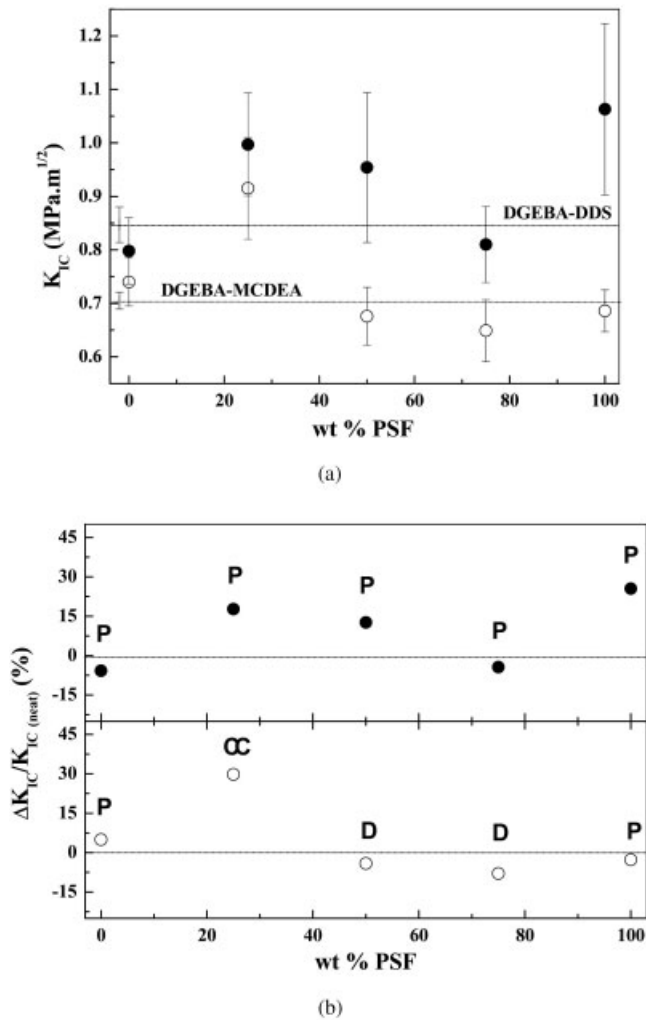


FIG. 3. Critical stress-intensity factor (K_{IC}) (a) and percent increase in K_{IC} ($\Delta K_{IC}/K_{IC} (neat)$) (b), as a function of the relative fraction of PSF for 10 wt% PSF/PEI modified DGEBA-DA systems: (●) DDS; (○) MCDEA; (dotted line) neat system. Morphology is indicated as: P, particulate; CC, co-continuous; D, "island" domains.

degassed under vacuum during 10 min to remove trapped air. The chosen curing schedules were 2 h at 200°C followed by 1 h at 220°C for DDS, and 4 h at 200°C followed by 2 h at 220°C for MCDEA, in order to reach full epoxy groups conversion. The cured plates were slowly cooled down to room temperature and removed from the mold to be machined, in order to produce rectangular bars for mechanical testing.

Mechanical Characterization

In order to measure flexural modulus, neat and modified epoxy unnotched specimens were tested in three-point bending configuration. The specimen cross-section was 5.5 mm \times 11 mm with a support span of 80 mm. Flexural modulus was determined following the ASTM D790M-93 standard recommendations [8] from the initial load-deflection slope as:

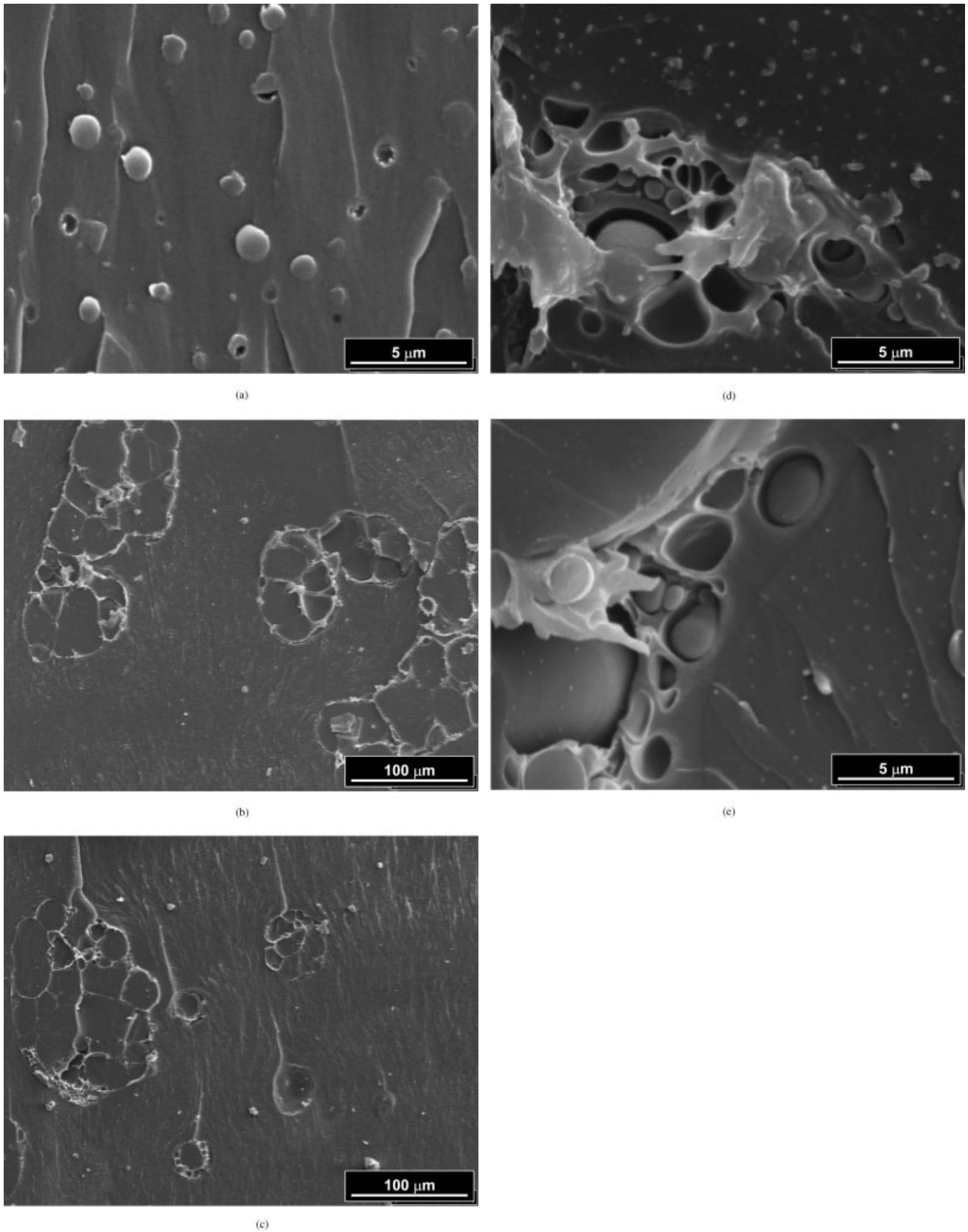


FIG. 4. SEM of fracture surfaces for 10 wt% PSF/PEI modified DGEBA-MCDEA systems in different PSF/PEI ratios: 0/100 (a); 25/75 (b); 50/50 (c); 25/75 higher magnification (d); and 50/50 higher magnification (e).

consequence of the higher rigidity of the DGEBA-DDS network.

For both the DDS and MCDEA blends, the variation of the PSF proportion in the TP mixture did not show a clear influence over modulus values, even though PEI modulus is higher than PSF one. Similar values were determined for modified and unmodified systems. Then, the loss of stiffness that is a necessary consequence of adding rubber particles is avoided when high T_g TPs are used.

The critical stress intensity factor, K_{IC} , and the relative toughness improvement ($\Delta K_{IC}/K_{IC(neat)}$), where $K_{IC(neat)}$ is the neat resin value) vs. wt% PSF for 10% of total TP data are plotted in Fig. 3, for DDS and MCDEA blends, and compared with the neat systems values (dotted line). For DDS cured samples the resulting morphologies are particulate, with TP rich particles dispersed in an epoxy-amine rich matrix, for all the PSF/PEI proportions. The replacement of part of the PEI by PSF regardless of the PSF/PEI proportion leads to a slight, practically constant, but clear increase in toughness. As an exception, the 75/25 blend, with an initial composition close to the miscibility limit, i.e., close to the composition where the samples are initially phase separated, does not show a significant change in K_{IC} value with respect to the neat system, probably due to the fact that a non-uniform particle distribution is present. As demonstrated before [11] for PSF/PEI ratios near the miscibility limit, slight temperatures changes provoked the generation of morphology gradients, even in initially homogeneous blends.

A quite different behavior is observed when MCDEA is used as hardener. Replacing 25% of PEI by PSF (25/75 mixture) drives to a substantial change in morphology, from a particulate type (0/100 blend) (Fig. 4a), to a structure where the DGEBA-MCDEA rich-phase is continuous and the TP rich phase shows co-continuity (Fig. 4b). This change in morphology leads to a 30% increase in toughness, as can be observed in Fig. 3b.

In these modified-epoxy blends, the crack is forced to advance through the TP-rich phase that is obviously tougher than the epoxy-rich phase leading to an increase in toughness [12]. On the other hand, it has been well established in literature [12, 13] that co-continuous microstructures are more effective in toughening than particulate morphologies.

Modification with 10 wt% PSF/PEI—50/50 and 75/25 ratios—leads to double-phase morphologies, characteristic of initially heterogeneous blends, consisting in macroscopic irregular co-continuous TP-rich domains (“island” domains) dispersed in an epoxy-rich matrix, containing dispersed TP-rich particles (Fig. 4c, 50/50). The TP-rich domains show morphologies where epoxy domains are connected by threads of TP. As it was pointed out in a previous work [14] based on X-ray microanalysis, this TP-rich phase may be ascribed to be composed of PEI. Ductile drawing of the TP-rich phase is

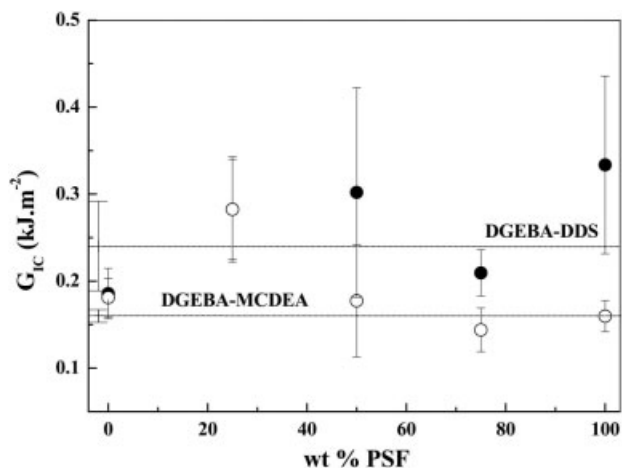


FIG. 5. Energy release rate at crack initiation (G_{IC}) as a function of the relative fraction of PSF for 10 wt% PSF/PEI modified DGEBA-DA systems: (●) DDS; (○) MCDEA; (dotted line) neat system.

also observed on the fracture surfaces of both blends with co-continuous and island domains morphologies (Fig. 4d and e). Therefore, crack bridging by these ductile phases is expected to contribute to the overall toughness. In addition, tails behind the island domains are clearly observed in Fig. 4c, evidencing the presence of the crack-pinning mechanism that also would consume additional energy [13–15]. However, based on SEM analysis of fracture surfaces only, we cannot identify the major toughening mechanism operating in our blends as demonstrated by Pearson and Yee [16]. Microcracking might also be occurring and crack bridging would contribute to toughening mostly by stabilizing the microcracks and, hence, by controlling the size of the microcracking zone [16].

Nevertheless, the increase in the PSF/PEI ratio does not drive to a toughness improvement, compared to the unmodified DGEBA-MCDEA system.

In addition, the energy release rate at crack initiation (G_{IC}) was calculated using K_{IC} and E values [9]:

$$G_{IC} = K_{IC}^2(1 - \nu^2)/E. \quad (4)$$

Poisson’s ratio (ν) was taken equal to 0.4 [15]. The obtained G_{IC} values vs. PSF wt% are plotted in Fig. 5. The tendency is similar to the one observed in K_{IC} curves.

A quite different behavior is observed when blends with 15 wt% of modifier and using MCDEA as hardener are polymerized at 200°C. For these systems a small increase in PSF/PEI ratio provokes a drastic change in morphology. While a mixture containing 15 wt% PEI shows a particulate morphology, blends with PSF/PEI ratio 5/95 and 10/90 develop phase-inverted and co-continuous morphologies, respectively. In the first of these two cases (5/95), epoxy-rich domains appear dis-

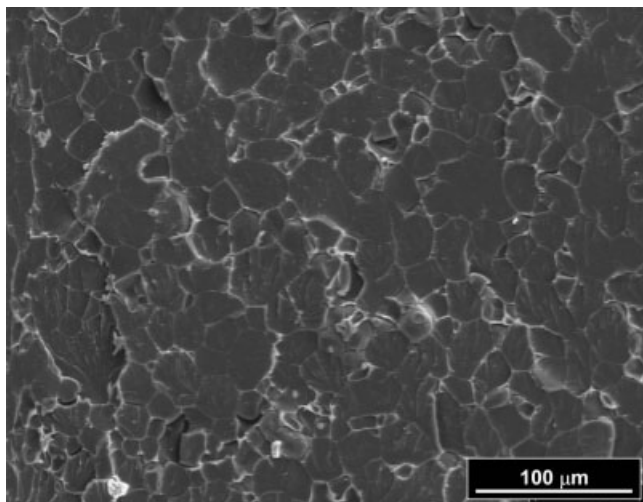


FIG. 6. SEM of fracture surface for 15 wt% PSF/PEI modified DGEBA-MCDEA system in 10/90 PSF/PEI ratio.

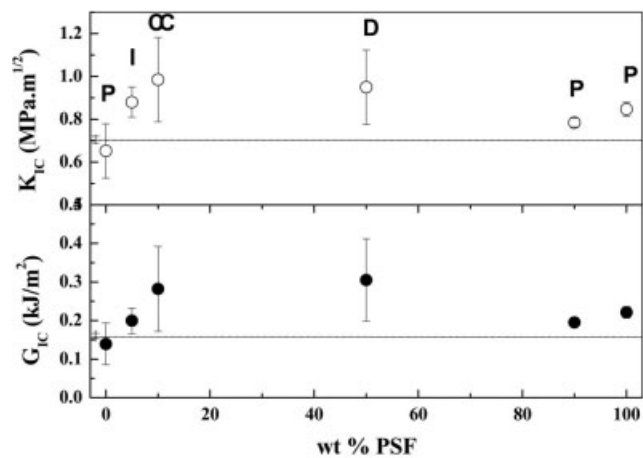
persed within a TP-rich matrix (not shown). In the second case (10/90), a cellular structure with certain degree of co-continuity is achieved (Fig. 6). When a plate of this composition was immersed in methylene chloride, it was swollen by the solvent, and the continuous phase and part of the epoxy-amine particles precipitated on it were extracted. However, the specimen kept its shape, confirming the existence of the above mentioned morphology.

The described changes in morphology also affect the materials fracture toughness (Fig. 7a and b). As Fig. 7b shows, replacing 5 and 10% of PEI by PSF, leads to a 25 and 40% enhancement in K_{IC} values, respectively. When a 15% mixture in a 50/50 PSF/PEI ratio is analyzed, fracture surfaces SEM micrographs show that the final structure is formed by a high concentration of phase-inverted PEI-rich domains with an average diameter between 200 and 700 μm (“island domains”) (Fig. 8), which lead to an improvement in fracture toughness of 35%. For a 90/10 blend (not shown) a particulate morphology is obtained again and, as would be expected, no noticeable enhancement in K_{IC} was observed.

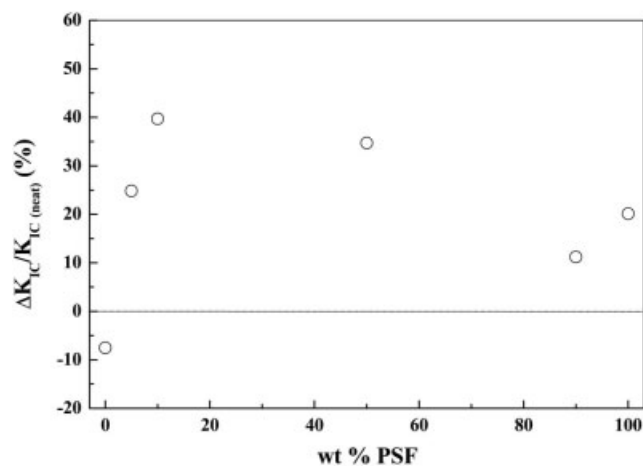
In agreement with the results obtained for 10 wt% of modifier, SEM analysis of the fracture surfaces confirms that the TP-rich phase undergoes ductile tearing; hence, crack bridging exists. Furthermore, tails near the island domains are observed in Fig. 8, suggesting that crack-pinning is also occurring in this microstructure and, hence, this mechanism would also contribute to the overall toughness for this composition.

CONCLUSIONS

We have analyzed the mechanical behavior of samples containing 10 and 15 wt% TP modifiers. We observed



(a)



(b)

FIG. 7. K_{IC} and G_{IC} (a) and percent increase in K_{IC} ($\Delta K_{IC}/K_{IC}(\text{neat})$) (b) as a function of the relative fraction of PSF for 15 wt% PSF/PEI modified DGEBA-DA systems: (●) DDS; (○) MCDEA; (dotted line) neat system. Morphology is indicated as: P, particulate; I, inverted; CC, co-continuous; D, “island” domains.

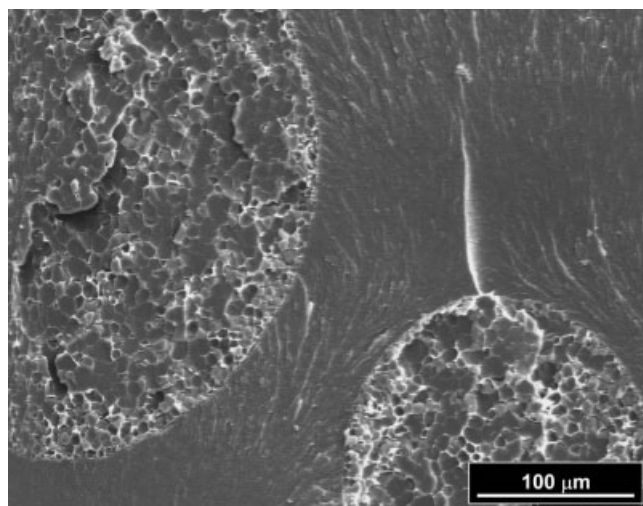


FIG. 8. SEM of fracture surface for 15 wt% PSF/PEI modified DGEBA-MCDEA system in 50/50 PSF/PEI ratio.

that when a small part of PEI is replaced by a second polymer like PSF, drastic changes in the final morphologies [14] and then in fracture properties were obtained when compared to the systems modified only with PEI.

When the TP-rich phase shows continuity, great improvements in toughness (up to 40%) are achieved. Hence, we can conclude that by varying PSF/PEI ratio, at a constant modifier total concentration, appropriate morphology changes can be induced. Therefore, materials with better fracture properties can be obtained, keeping formulations viscosity constant. As an additional advantage, no important changes in elastic modulus of final materials are found.

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