The toughening of epoxy resins with thermoplastics: 1. Trifunctional epoxy resin–polyetherimide blends

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A series of blends has been prepared by adding a polyetherimide, in varying proportions, to a trifunctional epoxy resin, triglycidylparaaminophenol, cured with 4,4'-diaminodiphenylsulphone. All the materials showed two-phase morphology when characterized by dynamic mechanical thermal analysis and scanning electron microscopy. Addition of the thermoplastic resulted in improved fracture properties (K_{1C} and G_{1C}), as measured by three-point bending experiments, although no obvious correlation with blend morphology was observed.

INTRODUCTION

There is an ever increasing demand for high performance composites, primarily for aerospace applications. The materials which serve as matrices for fibre-reinforced composites should possess high fracture toughness, high modulus and good high temperature behaviour. Of all the polymer thermosets, epoxies are most widely used, but, unfortunately, they tend to have a characteristic low resistance to brittle fracture. Rubber toughening of epoxies, predominantly using amino- and carboxyl-terminated butadiene–acrylonitrile elastomers, has met with some success[1-7] and commercial products based on this approach have been developed. However, the improvements in fracture toughness of these rubber-modified materials are invariably accompanied by a significant drop in modulus[5,7,8]. It has been suggested that in rubber toughened epoxies small rubber particles promote shear banding whereas large particles are responsible for crazing[3,4,9], with both mechanisms giving rise to an enhancement in fracture toughness. The best results for rubber toughening have been achieved with epoxies such as DGEBA[10,11], which have a relatively low crosslink density. The degree to which a highly crosslinked resin may be toughened is very limited since its ability to deform by shear yielding is reduced as the crosslink density increases[12,13].

More recently, attempts have been made to toughen highly crosslinked thermosetting polymers with high modulus, high glass transition temperature (T_g) thermoplastics. Such high performance thermoplastics should not compromise the desirable mechanical properties of brittle, glassy polymers and yet their inherent toughness should provide an enhancement in fracture properties, since thermoplastic toughening does not depend on matrix ductility. Several workers have investigated the modification of epoxy resins with polyethersulphones[14-19] and it is generally agreed that such materials show relatively modest improvements in mechanical properties compared with the corresponding unmodified epoxy resins, provided that phase separation and good interfacial adhesion occur[16,19]. Similar conclusions were reached with respect to epoxy resin–polyetherimide blends[20,21].

This paper concerns the toughening of a trifunctional epoxy resin using a commercial polyetherimide [PEI (Ultem 1000)]. The work is part of a project involving a wide ranging study of the factors which control the fracture toughness and other mechanical properties of blends of thermosets with high modulus thermoplastics. Further results will be presented in future publications.

EXPERIMENTAL

Materials

The trifunctional epoxy resin, triglycidylparaaminophenol [TGPAP (MY0510)], was cured with 27.5 wt% (38 phr) of 4,4'-diaminodiphenylsulphone [4,4'-DDS (HT976)]. The thermoplastic toughening agent was Ultem 1000, an amorphous polyetherimide (General Electric). This had a number average molecular weight of $18\,000$ g mol^{-1}. All the materials were characterized by n.m.r. and i.r. spectroscopies and then used as supplied, with no attempt at further purification.

Blending procedure

Resin systems containing 0–40 wt% of the thermoplastic were prepared using a standard procedure. The PEI was dissolved in dichloromethane (CH_2Cl_2) and mixed with the resin at room temperature. The solution was heated in an oil bath to $\sim 80°C$ to remove most of the solvent and then the hardener was dispersed in the resin–thermoplastic mixture. This was then poured into an open chrome steel mould (10×15 cm) which had been preheated to $140°C$ in a vacuum oven. The

remaining solvent was removed by degassing under vacuum for 30 min, before curing for 2 h at 180°C. Postcuring was carried out for 10 h at 200°C. Following both curing and postcuring the oven was switched off and the plaques allowed to cool slowly to room temperature in order to prevent cracking.

Instrumental procedures

Test samples for dynamic mechanical analysis ($\sim 30 \times 10 \times 3$ mm) and fracture testing ($\sim 80 \times 10 \times 3$ mm) were machined from these plaques, and the fracture specimens were machine notched. These central V-notches were sharpened by pressing a razor blade into the notch tip to give an overall notch depth of ~ 3 mm.

Dynamic mechanical data were acquired using a Polymer Laboratories dynamic mechanical thermal analyser at a frequency of 10 Hz in the single cantilever bending mode and at a heating rate of $2°C$ min^{-1}. Transition temperatures were taken from the peak maxima on the tan δ versus temperature plots.

Fracture mechanics measurements were obtained using a modified Nene MC3000 tensometer operated in the compression mode. The test samples were fractured at 23°C using a wedge-shaped striker and a three-point bending geometry. The span between the supports was 50 mm and the strain rate was 1 mm min^{-1}. Since the internal displacement gauge of the tensometer was not sufficiently sensitive for these experiments a transducer was clamped to the crosshead to measure displacement, and, hence, strain.

A Philips 525M instrument was used for scanning electron microscopy (SEM) and fracture surfaces were coated with gold using a Polaron E5000M sputter coater. Etching was carried out by immersing the fracture ends in refluxing CH_2Cl_2 for 6 h prior to sputtering.

RESULTS AND DISCUSSION

Dynamic mechanical analyses

Dynamic mechanical data for cured and postcured materials are presented in *Table 1* and examples are
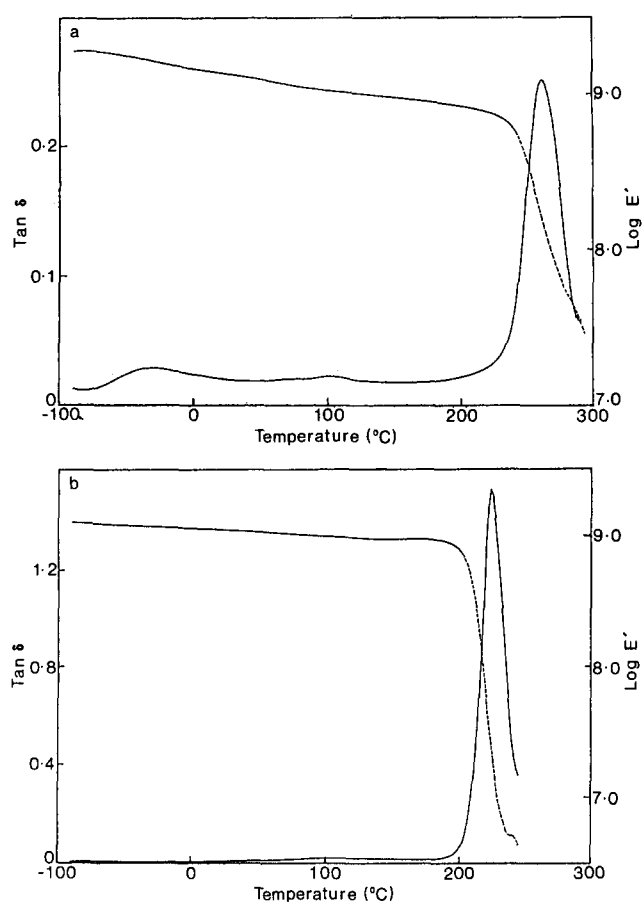

Figure 1 Dynamic mechanical data for (a) the neat epoxy resin and (b) PEI

illustrated in *Figures 1* and *2*. Data are also included for a compression moulded sample of the PEI as a reference. In all the blends it was possible to resolve separate α transitions in the tan δ versus temperature plots which could be attributed to the PEI and epoxy components, which is indicative of a heterogeneous morphology. It can be seen that the T_g of the unmodified resin is significantly lower than the epoxy glass transitions in the blends, particularly for the systems of higher ($>15\%$) thermoplastic content.

In the cured systems the PEI T_g is approximately constant for thermoplastic levels of 15% and greater, which corresponds to the onset of phase inversion (as discussed later). In all cases the thermoplastic T_g is believed to be significantly plasticized by unreacted TGPAP. When the blends were granulated and subjected to Soxhlet extraction (48 h) in boiling CH_2Cl_2 unreacted epoxy resin was extracted, as evidenced by ^1H n.m.r. spectroscopy.

Although, in general, postcuring has no significant effect on the temperature of the epoxy α transition, there is a significant increase in the temperature ($\sim 25°C$) of the PEI T_g on postcuring. This may arise from reaction between the epoxy and PEI (to form a graft copolymer), crosslinking of the thermoplastic, or loss of plasticizer.

The β transition, which can be attributed to restricted segmental motions within the network, shows no obvious trends. However, since previous studies[22] have shown that this transition is particularly sensitive to moisture content, it would be necessary to ensure that all the systems had the same hygrothermal history for a rigorous analysis to be meaningful.
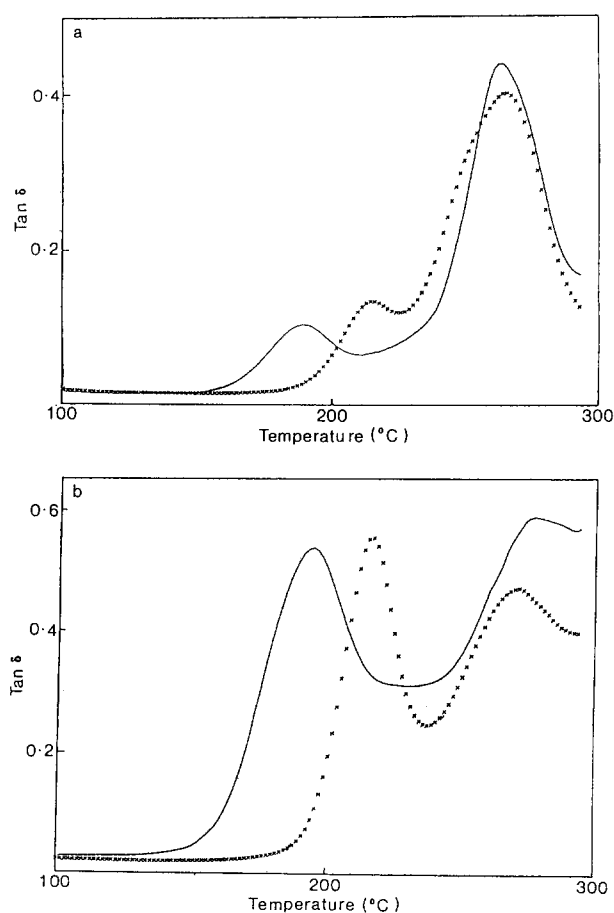
Table 1 Dynamic mechanical data for TGPAP/4,4'-DDS/PEI blends

| PEI (wt%) | Transition (°C) | | |
	β (epoxy)	α (PEI)	α (epoxy)
0 Cured	-30	–	262
Postcured	-24		260
10 Cured	-38	177	267
Postcured	-37	209	263
15 Cured	-33	190	263
Postcured	-31	215	265
20 Cured	-39	195	276
Postcured	-35	216	272
25 Cured	-34	193	274
Postcured	-38	218	272
30 Cured	-32	195	274
Postcured	-46	218	274
35 Cured	-24	198	276
Postcured	-28	215	269
40 Cured	-46	194	277
Postcured	-29	216	271
100		224	

Figure 2 Dynamic mechanical data for cured (—) and postcured (×) blends containing (a) 15 wt% PEI and (b) 40 wt% PEI

Fracture experiments

Although the samples studied did not fracture in a perfectly elastic manner, the mode of failure was sufficiently brittle to enable meaningful results to be obtained by treating the raw data using the LEFM theory[23]. Critical values of the stress intensity factor (K_{1C}) and the strain release rate (G_{1C}) are the average of at least six samples and were both calculated directly from the force–displacement curves using the following equations:

$$G_{1C} = U/BW\phi$$

$$K_{1C} = (3/2 \, S/BW^2)F_{max}Ya^{1/2}$$

where U is the energy absorbed at fracture, S is the span between supports, B is the specimen thickness, F_{max} is the force to fracture, W is the specimen depth, Y and ϕ are geometrical corrections and a is the notch depth.

The results of the fracture experiments are presented in *Table 2* and it can be seen that the standard deviations were relatively low for this type of measurement. Although the addition of 10% thermoplastic gives no improvement in fracture properties, increasing the PEI content to 15% results in a significant increase in toughness. However, there is no further improvement when the thermoplastic content is increased in the range 15–40%. The cured and postcured systems show the same trends in fracture properties, and postcuring is clearly beneficial.

Scanning electron microscopy

All the epoxy–PEI blends were examined by SEM and although heterogeneity was observed in all cases, marked

changes in morphology were noted, of which some typical examples are shown in *Figures 3–7*. Where possible, the samples were etched in refluxing CH_2Cl_2. Materials with a high PEI content (>15%) which had not been postcured did not survive this treatment. It was, however, possible to etch all the postcured materials except the 40% PEI blend.

The fracture surface of the 10% PEI blend (*Figure 3*) consists of a continuous epoxy matrix with extensive

Table 2 Fracture data for TGPAP/4,4'-DDS/PEI blends

| PEI (wt%)		K_{1C} (MN m$^{-3/2}$)	G_{1C} (kJ m^{-2})
0	Cured	0.79 (0.09)	0.23 (0.03)
	Postcured	1.49 (0.13)	0.66 (0.10)
10	Cured	0.73 (0.12)	0.19 (0.04)
	Postcured	1.22 (0.17)	0.43 (0.11)
15	Cured	1.78 (0.17)	1.13 (0.16)
	Postcured	1.73 (0.11)	0.93 (0.14)
20	Cured	1.58 (0.03)	0.76 (0.02)
	Postcured	1.97 (0.05)	1.14 (0.06)
25	Cured	1.68 (0.03)	0.87 (0.03)
	Postcured	2.13 (0.07)	1.31 (0.08)
30	Cured	1.73 (0.04)	0.89 (0.04)
	Postcured	2.14 (0.07)	1.35 (0.09)
35	Cured	1.66 (0.03)	0.88 (0.04)
	Postcured	2.10 (0.07)	1.26 (0.09)
40	Cured	1.63 (0.06)	0.84 (0.03)
	Postcured	2.06 (0.06)	1.26 (0.06)

Standard deviations in parentheses
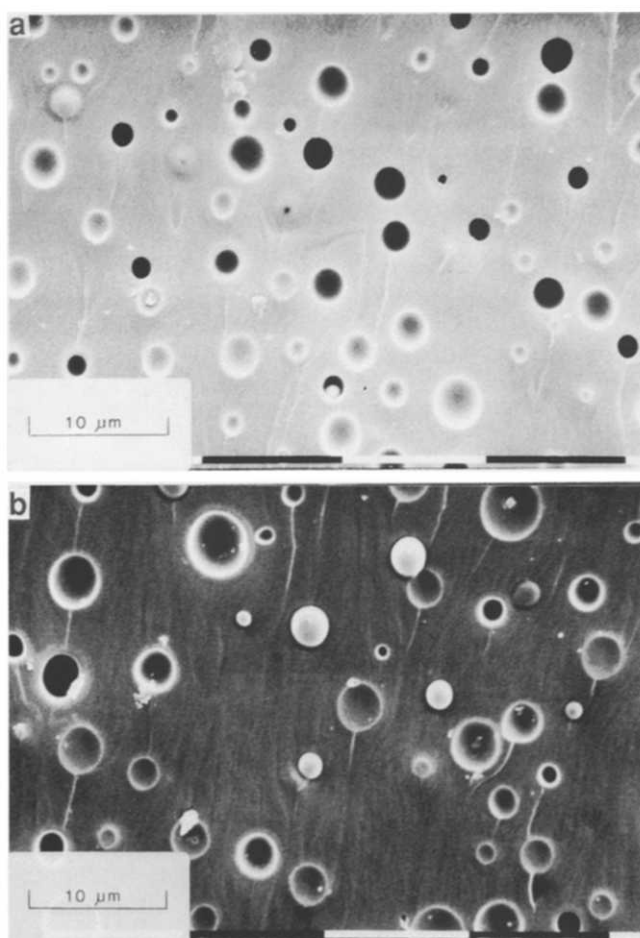
Figure 3 Scanning electron micrographs of a blend containing 10 wt% PEI etched in CH_2Cl_2: (a) cured; (b) postcured
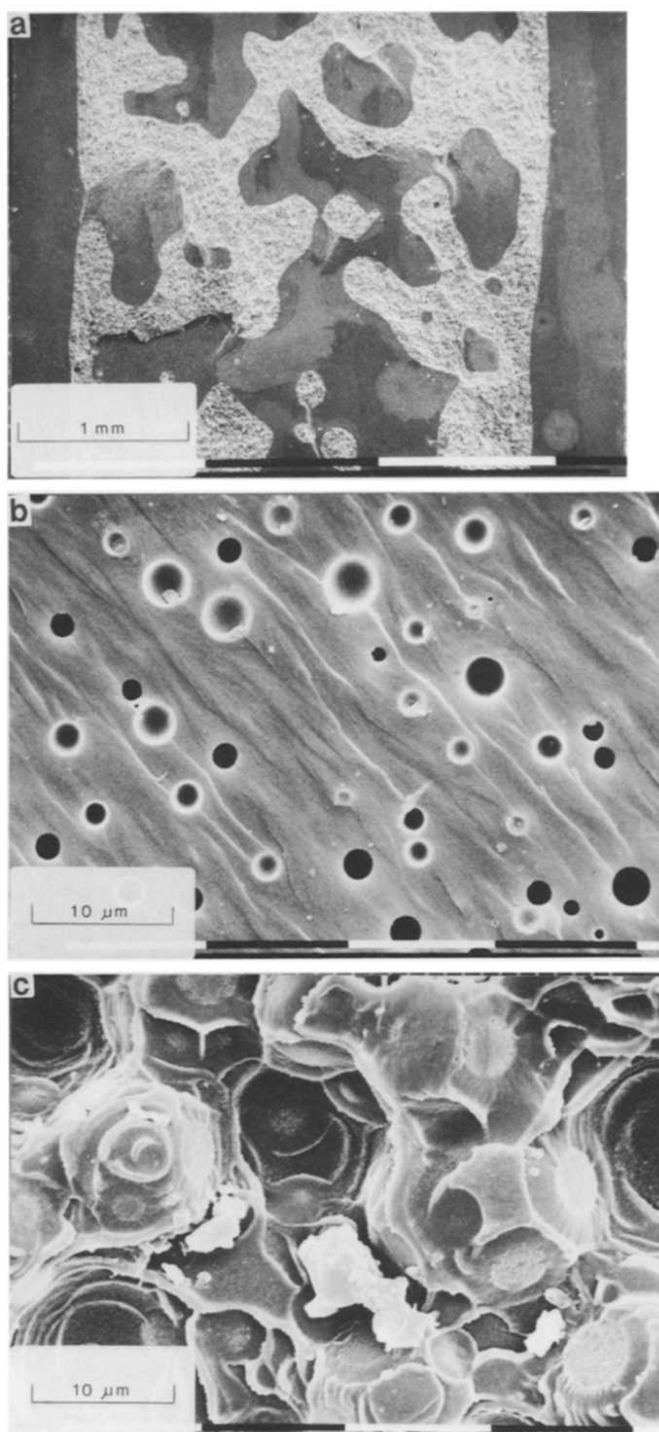
Figure 4 Scanning electron micrographs of a cured blend containing 15 wt% PEI: (a) 'sandwich' morphology; (b) continuous epoxy region, etched in CH_2Cl_2; (c) continuous thermoplastic region

The 20% PEI blend (*Figure 5*) shows complete phase inversion, and has a honeycomb morphology which is not seen in the other systems of this series. The epoxy domains (50–100 μm in diameter) are connected by threads of PEI. In the cured materials these threads are completely dissolved during the etching process, resulting in disintegration of the sample. However, the corresponding postcured blend retains structural integrity in boiling CH_2Cl_2, although some thermoplastic is lost from the surface. The 25% PEI material (*Figure 6*) is also
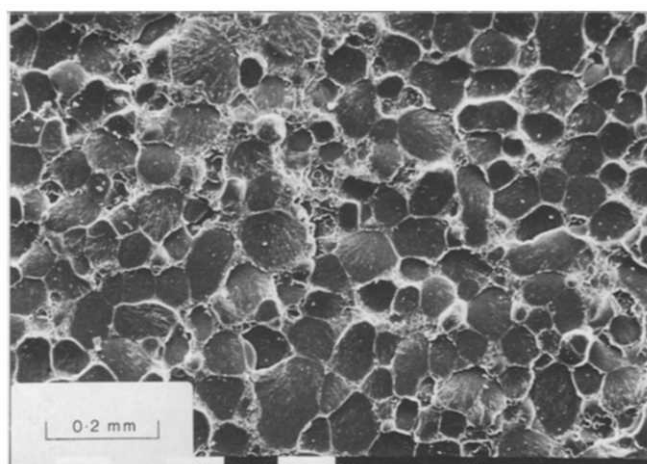

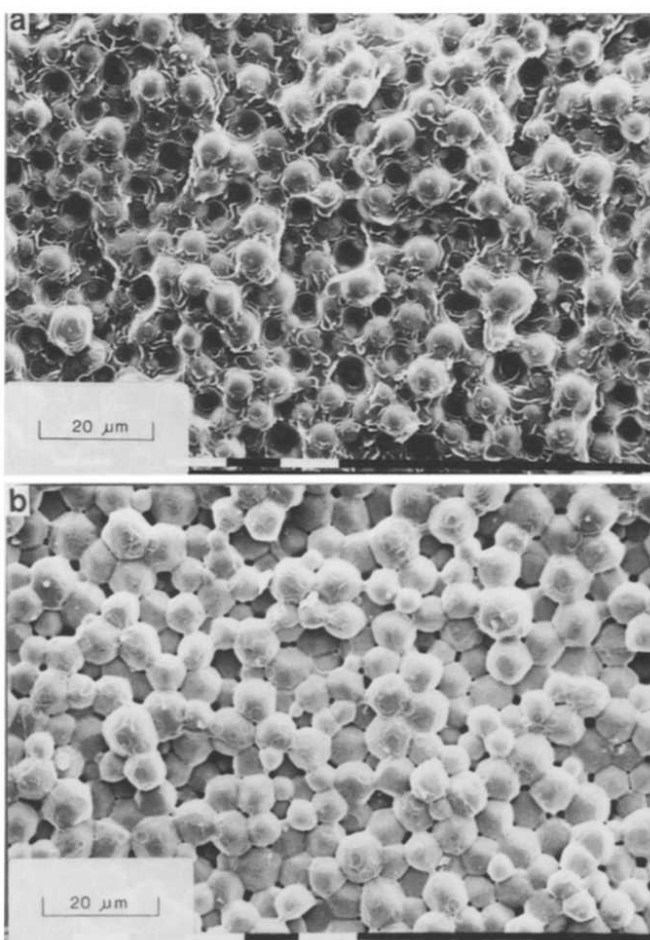Figure 5 Scanning electron micrograph of a postcured blend containing 20 wt% PEI

Figure 6 Scanning electron micrographs of a blend containing 25 wt% PEI: (a) cured; (b) postcured, etched in CH_2Cl_2
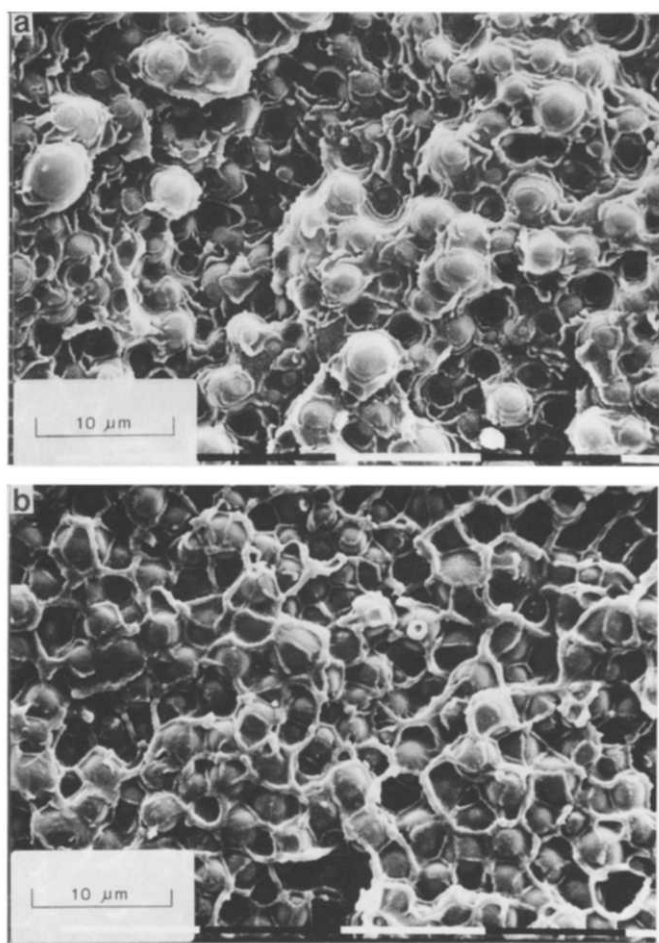
shear banding, as described by Bucknall and Marchetti[24], between dispersed PEI domains of ~2–3 μm diameter and although most of the thermoplastic is etched from the surface of the postcured blend, a few spherical inclusions remain. The continuous epoxy phases of the 10% and 15% PEI materials are indistinguishable from each other (*Figures 3a* and *4b*), although in the latter blend there are regions of phase inversion (~1 mm) and there is also a pronounced skin of continuous epoxy material (~0.4 mm thick) as shown in *Figure 4a*. The phase inverted regions appear to consist of epoxy domains wrapped in layers of thermoplastic (*Figure 4c*).

Figure 7 Scanning electron micrograph of a blend containing 40 wt% PEI: (a) cured; (b) postcured

completely phase inverted and has a morphology which is similar to that of the phase inverted regions of the 15% blend. Where the thermoplastic forms the continuous phase, the micrographs show that it is plastically deformed during the fracture process. This ductile tearing/drawing of the PEI is particularly evident in *Figures 4c* and *7b*. The epoxy domains in the 25% PEI blend are $\sim 5–10\ \mu m$, compared with $15–20\ \mu m$ in the 15% PEI material, and although the 30% and 40% (*Figure 7*) PEI blends have morphologies similar to that of the 25% PEI system the epoxy domains are even smaller ($\sim 3–5\ \mu m$).

The micrographs show clearly why the K_{1C}/G_{1C} values do not increase significantly when the PEI content exceeds 15%, since all these blends have a continuous thermoplastic matrix. The surface area of PEI generated during fracture is therefore essentially the same in each case. It is also evident that the growing crack propagates around, rather than through, the epoxy domains in the phase inverted blends. In the cured materials the surfaces of the epoxy regions are relatively free of thermoplastic (*Figure 7a*), whereas in the postcured materials the crack appears to have propagated through the thermoplastic rather than around the matrix–particle interface (*Figure 7b*). This would explain why postcuring significantly increases the toughness of the blends, since the strength of the matrix–particle interface is known to increase during postcure. This is evidenced by the markedly improved solvent resistance of the postcured blends when etching using CH_2Cl_2.

CONCLUSIONS

All the blends prepared exhibited heterogeneity, and their morphology alters considerably with thermoplastic content. Phase inversion occurs when the PEI content is $\sim 15\ wt\%$ or greater. However, there seems to be no direct correlation between fracture properties and the morphological changes, although there is a significant increase in toughness when PEI forms the continuous phase.

Postcuring the blends invariably leads to an increase in the T_g of the thermoplastic phase. This is likely to be a result of a reduction in the plasticization of the PEI by the epoxy resin, since unreacted monomer will diffuse to the thermosetting regions during the additional heating. The postcuring temperature of 200°C is greater than the T_g of the PEI in the cured blends. The thermoplastic will therefore be sufficiently mobile during the postcuring process to allow this diffusion to take place. The fact that relatively little PEI can be extracted from most of the postcured blends indicates that a limited amount of covalent reaction occurs between the two components during postcure.

The improvement in fracture properties appears to arise predominantly from ductile tearing of the thermoplastic. It is unlikely that the fracture properties of epoxy resins with high crosslink density can be greater enhanced since they have intrinsically low yield stresses.

ACKNOWLEDGEMENTS

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