Toughening tetrafunctional epoxy resins using polyetherimide

Clive B. Bucknall and Adrian H. Gilbert
Cranfield Institute of Technology, Cranfield, Bedford MK43 0AL, UK
(Received 22 April 1988; revised 19 August 1988; accepted 23 August 1988)

Toughened epoxy resins have been prepared by dissolving polyetherimide (PEI) in a tetraglycidyl-4,4′-diaminodiphenyl methane (TGDDM) based resin with 30 p.h.r. diaminodiphenyl sulphone (DDS) as curing agent. The polyetherimide forms a separate phase, with a dynamic loss peak which varies between 200 and 212°C. The loss peak of the resin occurs at about 265°C. Three-point bend tests show a linear increase in K_{IC} with PEI content, from 0.5 MPa$\sqrt{m}$ in the parent resin to 1.42 MPa$\sqrt{m}$ at 25 p.h.r. of PEI. Young's modulus at 23°C shows a modest reduction from 3.6 to 3.5 GPa over the same composition range.

(Keywords: epoxy resin; polyetherimide; blend; toughening; phase separation; dynamic loss)

THE PROBLEM

Highly cross-linked thermosetting resins are difficult to toughen. The well established technology of rubber toughening is effective for difunctional resins such as the diglycidyl ether of Bisphenol A (DGEBA), but as the cross-link density increases and the resin therefore becomes even less ductile, rubber particles become progressively less able to increase fracture resistance. The relationship between cross-link density and strengthening capability has been most clearly demonstrated by the work of Yee and Pearson[1], which is illustrated in *Figure 1*. In the absence of rubber modification, variations in the molecular weight between cross-links M_c have little effect on G_{IC}, but when 10 p.h.r. of a suitable rubber is added to the formulation, G_{IC} increases linearly with M_c.

The reasons for these effects of cross-link density are well known. Rubber toughening of thermosetting resins depends upon deformation in the resin matrix, which is usually accompanied by cavitation within the rubber particles[2,3], and consequent stress whitening of the yield zone. In the absence of such cavitation, yielding is highly constrained. As the resin matrix is cross-linked more tightly, its capacity to deform by shear yielding is reduced, and G_{IC} falls to that of the unmodified matrix. This observation proves that crack bridging by rubber particles[4] contributes very little to energy absorption during fracture.

In view of this inherent problem in causing yielding in highly cross-linked resins, it appears that successful toughening can be achieved only by introducing energy absorption processes that do not depend upon matrix ductility. The present paper discusses one such process, in which a high-performance ductile thermoplastic provides the toughening.

EXPERIMENTAL

Materials

The epoxy resin used throughout this work was Ciba-Geigy MY720 resin, which consists essentially of tetraglycidyl 4,4′-diaminodiphenyl methane. The resin was cured with 30 p.h.r. of diaminodiphenyl sulphone (Ciba-Geigy hardener HT 976). The modifier studied was General Electric's Ultem 1000 polyetherimide[5], an amorphous thermoplastic which has $M_n = 12\,000$ and $M_w = 30\,000$[6].

Resin compositions containing 0 to 30 p.h.r. of the thermoplastic were prepared by a standard procedure. The PEI was dried at 120°C under vacuum for 24 h before being dissolved in methylene chloride (CH_2Cl_2) and mixed with the resin at room temperature. The solution was heated slowly in an oil bath to 100°C to drive off most of the CH_2Cl_2, the remainder being removed under vacuum at 100°C. At this stage the solutions are clear, homogeneous, viscous liquids. At PEI concentrations above about 15 p.h.r. the solutions are glassy at room temperature.

The PEI solution was heated in an oil bath to 135°C, and the DDS hardener was added slowly with stirring over about 20 min. The resin was then cast into 30 × 30 × 3 mm sheets, using a parallel glass plate mould treated with Freekote 44 release agent. Degassing was carried out under vacuum at 100°C for 7 h, followed by curing for 16 h at 120°C, 2 h at 150°C and 2 h at 180°C, with post-curing for 4 h at 200°C. Finally, the oven was switched off and the cured sheet was allowed to cool very slowly to room temperature in order to avoid cracking.

Pellets of the neat PEI were compression moulded at 270°C into 30 × 30 × 6 mm sheet.

Testing

Specimens for mechanical testing were machined from sheet prepared as described above. Dynamic mechanical measurements at 10 Hz were made in the single cantilever bending mode between −80 and 300°C, using a Polymer Laboratories DMTA machine. The specimen cross-section was 10 × 1.4 mm with a span of 14 mm. Unnotched 60 × 10 × 3 mm bars were used at a span of 48 mm to measure flexural modulus at 23°C, according to ASTM D790[7].

Fracture mechanics measurements were made at 23°C in three-point bending at a crosshead speed of

0032-3861/89/020213-05$03.00

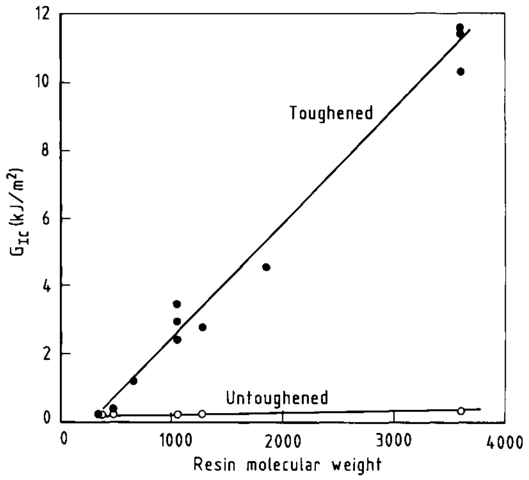

Figure 1 Effects of 10 p.h.r. of CTBN rubber on toughness of epoxy resins of differing cross-link densities (after Yee and Pearson[1])

1.3 mm min^{-1}, on sharply notched rectangular bars measuring 40 × 6 × 3 mm with a span of 24 mm. In the case of the neat PEI, the specimen dimensions were increased to 60 × 12 × 6 mm with a span of 48 mm, in order to ensure plane strain conditions in accordance with ASTM E399[8]. Central vee-notches were machined in the bars, and extended by pressing a fresh razor blade into the tip of the notch to give a crack length of 3.0 ± 0.3 mm.

Fracture surfaces were coated with gold/palladium and examined in the scanning electron microscope. Where solvent etching of the fracture surfaces was required, specimens were immersed in methylene chloride at 23°C for 24 h before applying the coating.

Specific gravities of the unmodified epoxy resin and of compression moulded PEI were measured by a displacement method using distilled water[9], in order to calculate volume concentrations in the cured blends.

RESULTS

Dynamic mechanical tests

Dynamic mechanical data for the unmodified resin, compression moulded polyetherimide and a material containing 20 p.h.r. of PEI, are compared in *Figure 2*. The unmodified resin gives two loss peaks: a low, broad secondary peak at about −45°C and a primary peak, corresponding to the glass transition, at 265°C. The principal feature in the PEI curve is the glass transition at 221°C.

Cured blends show three loss peaks which correspond approximately to those in the unmixed component polymers, showing that substantial demixing occurs during the curing reaction. The alpha transition in the resin is marked by a peak which occurs at temperatures between 261 and 267°C; the broad beta peak appears at about −45°C, as in the unmodified resin. The loss peak due to the glass transition in the PEI phase varies between 200 and 212°C, but shows no systematic dependence upon composition.

The effects of PEI content on the temperature of the two high-temperature peaks are illustrated in *Figure 3*. Volume concentrations of PEI given in this and subsequent figures are based on measured specific gravities for the cured MY720/DDS resin and for PEI of 1.37 and 1.32, respectively, at 23°C. The resin peak shows a small amount of scatter around a mean value of 265°C, but remains effectively unchanged by the addition of polyetherimide. Peak temperatures for the PEI lie between 10 and 20°C below the peak for the neat Ultem, showing more scatter than those of the resin, but at a mean value that appears to be independent of PEI concentration. Clearly, some interaction between the two phases, or plasticization by one of the low-molecular weight species in the blend, affects the relaxation of the thermoplastic phase, but the main feature of the dynamic mechanical data is the evidence for a high degree of phase separation.

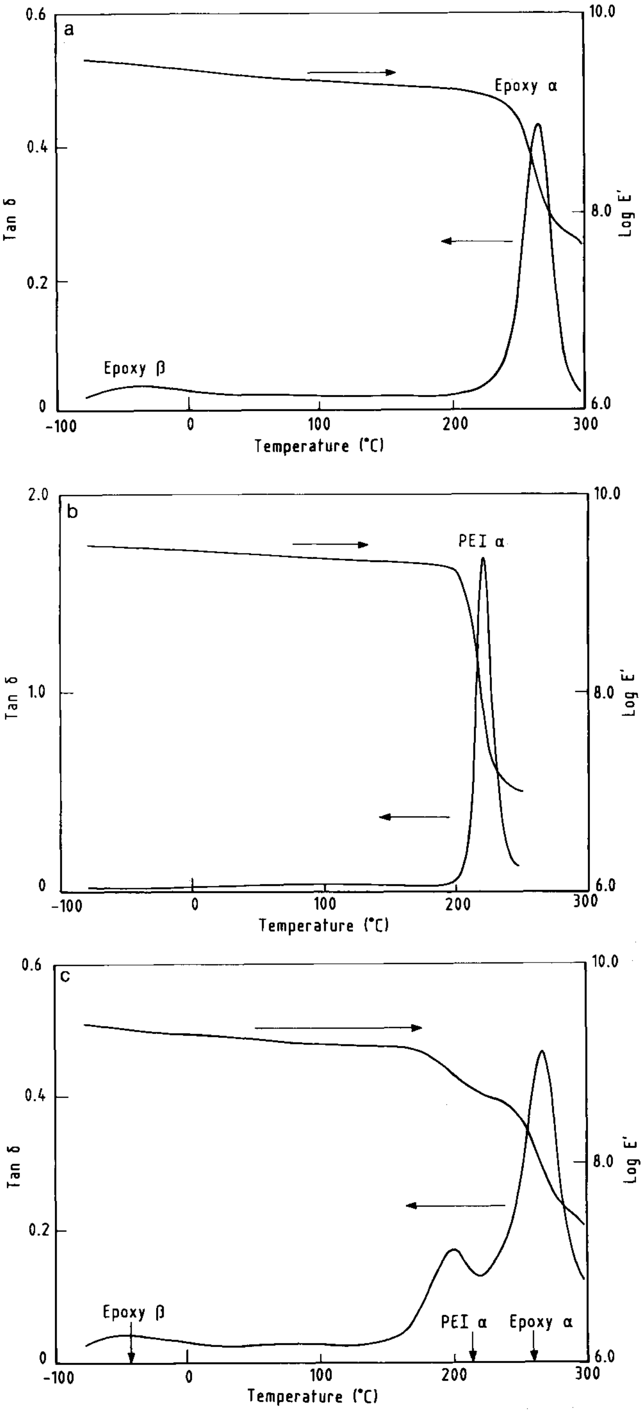

Figure 2 Dynamic mechanical data at 10 Hz for (a) the neat epoxy resin; (b) polyetherimide; and (c) a blend containing 20 p.h.r. of polyetherimide. Temperatures of tan δ peaks from (a) and (b) are shown on abscissa in (c)

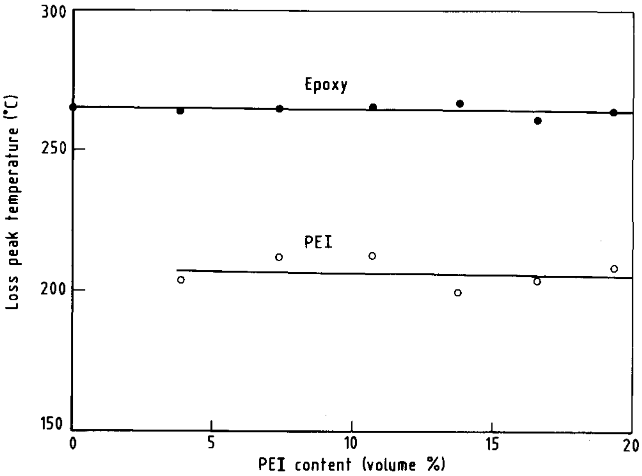

Figure 3 Effects of PEI content on temperature of tan δ peaks due to T_g in epoxy resin and PEI in phase-separated blends

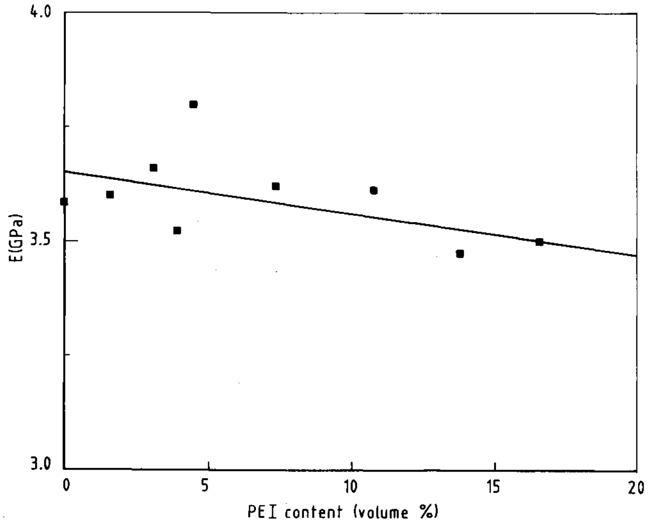

Figure 4 Effects of PEI content on Young's modulus of blends. $T = 23°C$

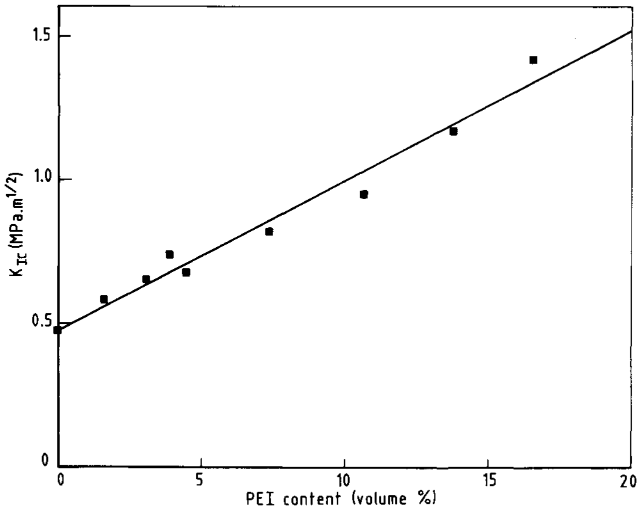

Figure 5 Effects of PEI content on K_{IC} of blends at 23°C

Flexural modulus

Flexural modulus at 23°C is plotted against polyetherimide concentration in *Figure 4*. Over the composition range studied, the modulus shows a slight decrease from 3.6 GPa in the epoxy resin to 3.5 GPa in a blend containing 25 p.h.r. of PEI.

Fracture mechanics

The relationship between K_{IC} and PEI content is essentially linear, as shown in *Figure 5*, in which each data point represents the mean of at least six tests. There is some scatter in the data, but it is not large for this type of measurement. Linear regression analysis gives a correlation coefficient of 0.99. Measurements on unblended PEI gave a K_{IC} value of 3.6 MPa$\sqrt{\text{m}}$.

The toughening effect of the polyetherimide is illustrated more dramatically in *Figure 6*, in which G_{IC} data are presented. These were obtained from K_{IC} using the relationship:

$$K_{IC}^2 = EG_{IC}/(1 - \nu^2) \qquad (1)$$

where Poisson's ratio ν was taken as 0.4 for all materials. This figure is an average obtained from a series of creep tests. In terms of G_{IC}, addition of 25 p.h.r. of PEI (equivalent to 16.6 vol %) raised toughness by a factor of eight.

Scanning electron microscopy

An examination of solvent-etched fracture surfaces shows that at PEI concentrations below 5 p.h.r. the thermoplastic phase is uniformly distributed as discrete spherical particles which are below 2 μm in diameter, as shown in *Figure 7*. At higher additive concentrations, the

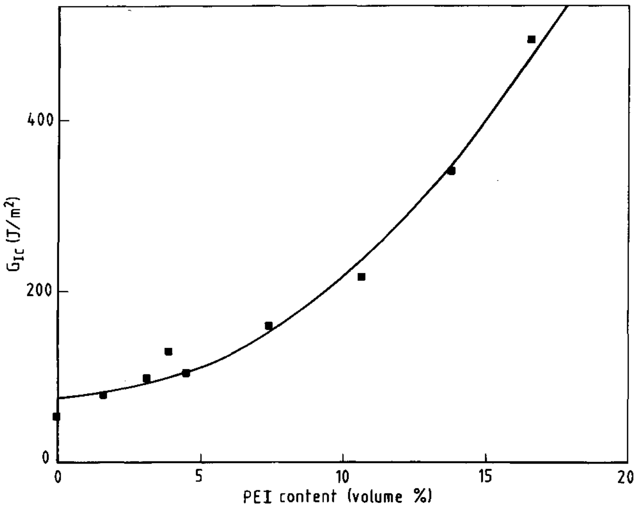

Figure 6 Effects of PEI content on G_{IC} of blends at 23°C

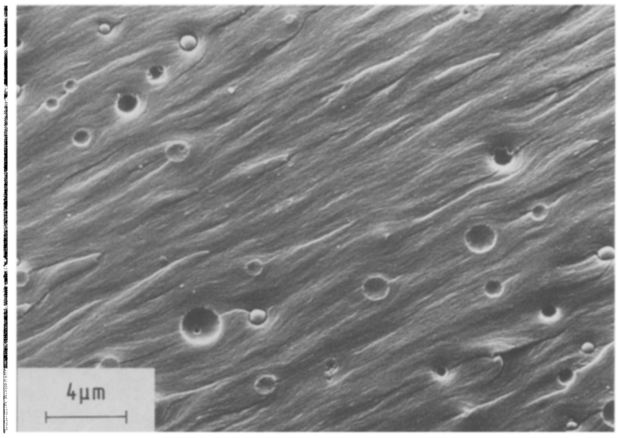

Figure 7 Fracture surface of blend containing 4 p.h.r. of PEI, after etching in methylene chloride

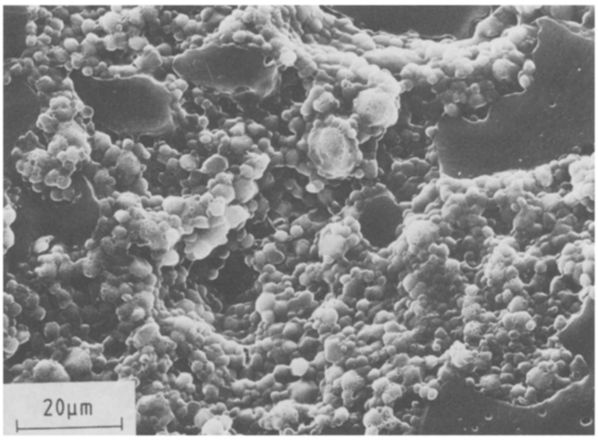

Figure 8 Fracture surface of blend containing 20 p.h.r. of PEI, etched in methylene chloride

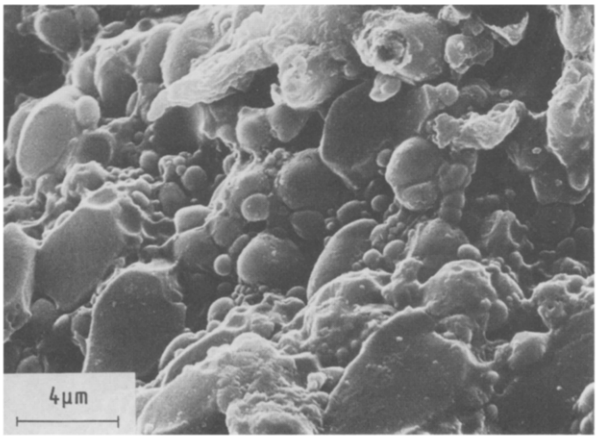

Figure 9 Fracture surface of blend containing 30 p.h.r. of PEI, etched in methylene chloride

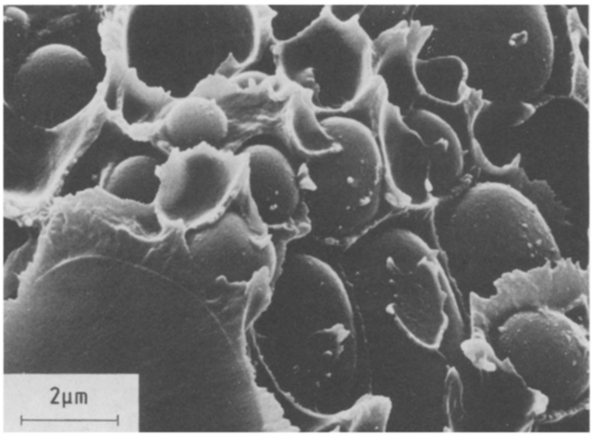

Figure 10 Fracture surface of blend containing 20 p.h.r. of PEI, unetched. Note evidence of drawing in the PEI

thermoplastic phase forms much larger, irregularly shaped domains, the sizes of which vary with curing conditions. An example of this type of structure in a blend containing 20 p.h.r. of PEI is presented in *Figure 8*. The domain size increases with PEI concentration. At 30 p.h.r. of PEI, the thermoplastic phase effectively forms the matrix and the epoxy resin becomes the disperse phase.

Etching with methylene chloride causes the PEI on the fracture surface to dissolve, leaving deep etch pits. An example of such an etched surface from a blend containing 30 p.h.r. of polyetherimide is shown in *Figure 9*. The solubility of the thermoplastic additive proves that it has not been cross-linked by the resin. Consequently, its ductility should be unimpaired.

Close examination of unetched specimens shows clear evidence of ductile drawing on the fracture surface, which occurs in the PEI domains. *Figure 10* shows a region in which drawing has taken place in this way.

DISCUSSION

This work has shown that addition of a thermoplastic can substantially increase the fracture toughness of highly cross-linked thermosetting resins. Specifically, addition of polyetherimide increases the toughness of the tetrafunctional epoxy resin TGDDM. Furthermore, reductions in the stiffness of the resin become significant only at temperatures above 180°C, where the additive approaches its own glass transition. The degree of improvement in G_{IC} is comparable with those reported by Diamant and Moulton in a survey of TGDDM blends containing a wide range of thermoplastic additives[10], and greater than that reported by Kim and Brown for a less highly cross-linked epoxy resin, which in the unmodified condition had a G_{IC} of 174 J/m^2 (ref. 11).

The technique of thermoplastic modification offers two advantages over more conventional rubber-toughening processes: it operates in thermosetting resins that are too tightly cross-linked to absorb significant amounts of energy by yielding; and it avoids the loss of modulus that is a necessary consequence of adding rubber particles. The work of Yee and Pearson has shown that rubber toughening becomes progressively less effective as cross-link density is increased[1], and previous attempts to toughen TGDDM resins with rubber have achieved no more than a doubling in G_{IC}[12].

The key to toughness in resin–plastic blends appears to be good phase separation. The dynamic mechanical data show that there is relatively little miscibility between the two components during the later stages of curing: there are two distinct high-temperature loss peaks corresponding to the T_g of resin and thermoplastic, and the temperatures of both the resin and PEI peaks are almost independent of the composition of the blend.

These results are in marked contrast to those obtained by Bucknall and Partridge in their study of polyethersulphone (PES) as a modifying agent for the same TGDDM/DDS resin formulation[13]. They found that PES did not separate as a discrete phase during curing, and did not significantly increase K_{IC} of the resin.

As PEI is added to the TGDDM/DDS resin, the relative size of the two high-temperature peaks changes, as might be expected. *Figure 11* shows that at 5 p.h.r. the thermoplastic peak is a small feature on the shoulder of the main resin peak; whereas at 30 p.h.r., the PEI peak approaches that of the resin in area and height, reflecting the large alpha peak of PEI itself (see *Figure 2*). *Figure 12* illustrates the influence of increasing PEI content on the modulus of the blend at elevated temperatures.

Despite the observed changes in morphology and domain size of the blends with composition, G_{IC} and K_{IC} increase smoothly with PEI content. This suggests that a single toughening mechanism operates over the whole of this composition range, and that the morphological

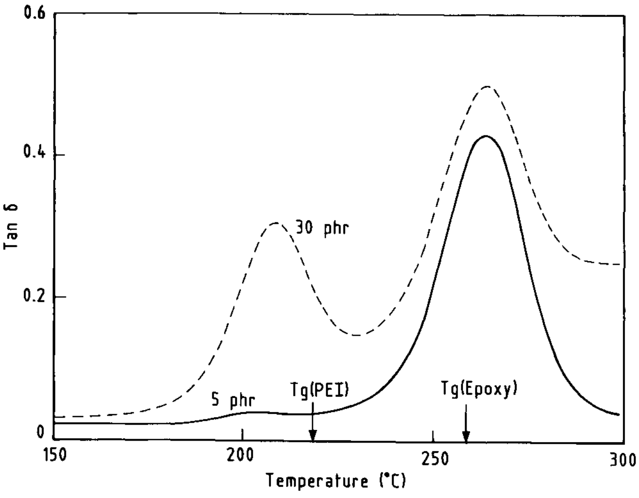

Figure 11 Comparison of tan δ curves at 10 Hz for blends containing 5 and 10 p.h.r. of PEI. Peak temperatures for neat PEI and epoxy resin are shown on abscissa

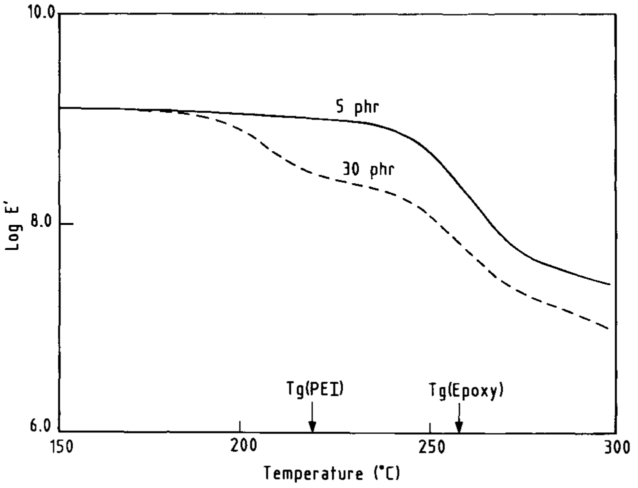

Figure 12 Comparison of dynamic modulus data at 10 Hz for blends containing 5 and 30 p.h.r. of PEI. Peak temperatures for neat PEI and epoxy resin are shown on abscissa

changes do not cause step changes in fracture behaviour of the type that has recently been reported in toughened nylons[14]. Scanning electron microscopy shows clear evidence of ductile tearing in the thermoplastic phase, and it must therefore be concluded that most of the energy absorption occurs in the modifier. According to this view, the first stage of fracture is brittle failure of the continuous resin phase, leaving the more ductile PEI bridging the gap. The fracture surface provides clear evidence that crack advance is delayed by the PEI domains.

The toughening effect of a minor amount of PEI is much greater than predicted by a simple rule of mixtures. Assuming that the effects of resin and modifier are additive, we can write:

$$K_{\mathrm{IC}}(\phi)=(1-\phi)K_{\mathrm{ICr}}+\alpha\phi K_{\mathrm{ICm}} \qquad (2)$$

where $K_{\mathrm{IC}}(\phi)$ is the fracture toughness of a blend containing a volume fraction ϕ of thermoplastic modifier, K_{ICr} and K_{ICm} are the (plane strain) toughnesses of neat resin and modifier, and α is an efficiency factor for the modifier. The equation reduces to the rule of mixtures when $\alpha=1.0$. The experiments summarized in *Figure 5* give a relatively high α value of 1.6, which probably derives from the lack of constraint in the PEI phase during fracture. If the thermoplastic forms bridges between opposing crack surfaces, it will not subsequently fail under plane strain conditions.

The observed drawing of the PEI phase can occur only when the resin–plastic interface is sufficiently strong to withstand the loads placed upon it. In the present work, interfacial strengths are clearly adequate, although no attempt was made to increase them by introducing reactive groups into the modifier. Either van der Waals bonding or other physical interactions are sufficient, or there are groups on the polymer which react with epoxy resin. A recent paper by Sefton *et al.*[15] refers to the importance of establishing a strong interface between phases; unfortunately, neither resin nor additive is identified in their paper.

Kim and Brown concluded that yielding in the resin matrix was the principal mechanism of toughening when concentrations up to about 10 wt% of a plastics modifier were added to their less highly cross-linked epoxy resin[11]. In this respect, their mechanism is similar to those found in corresponding rubber-toughened resins. At modifier contents between 10 and 30 wt%, Kim and Brown observed a phase inversion, which resulted in a change in toughening mechanism, and at 30 wt%, electron microscopy showed evidence of ductile drawing in the thermoplastic additive. The resin used in the present study is too highly cross-linked to permit yielding of the epoxy matrix, as suggested by Kim and Brown, and appears to depend largely for the toughness of its blends upon a drawing mechanism in the additive.

ACKNOWLEDGEMENTS

The authors thank the American Cyanamid Company for their support of this work, and for permission to publish this paper.

REFERENCES

1 Pearson, R. A. and Yee, A. E. 'Tough Comp. Mater. Rec. Dev.', 157–177, Noyes Publishing, Park Ridge, NJ, USA, 1987
2 Bascom, W. D., Cottington, R. L. and Jones, R. L. *J. Appl. Polym. Sci.* 1975, **19**, 2545
3 Pearson, R. A. and Yee, A. F. *Polymer* 1986, **21**, 2475
4 Kunz-Douglas, S., Beaumont, P. and Ashby, M. F. *J. Mater. Sci.* 1980, **15**, 1109
5 Relles, H. M. in 'Contemporary Topics in Polymer Science' (Ed. E. J. Vandenberg), Vol. 5, Plenum Press, New York, 1984
6 General Electric Company. Product literature on Ultem®
7 ASTM D790–81
8 ASTM E399–78a
9 ASTM D792–66
10 Diamant, J. and Moulton, R. J. 29th National SAMPE Symposium, 3–5 April 1984
11 Kim, S. C. and Brown, H. R. *J. Mater. Sci.* 1987, **22**, 2589
12 Lee, B. L., Lizak, C. M., Riew, C. K. and Moulton, R. J. SAMPE Techn. Conference, 7–9 October 1980
13 Bucknall, C. B. and Partridge, I. K. *Polymer* 1983, **24**, 639
14 Wu, S. *Polymer* 1985, **26**, 1855
15 Sefton, M. S., McGrail, P. T., Peacock, J. A., Crick, R. A., Davies, M. and Almen, G. in 'Polymers for Composites', Plastics and Rubber Institute, London, 1987