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Miscibility and fracture behaviour of epoxy resin–nitrated polyetherimide blends

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Nitrated polyetherimide (NI-PEI) was obtained by chemically modifying a commercially available polyetherimide (PEI) and was characterized by nuclear magnetic resonance and infra-red spectroscopies, elemental analysis and viscometry. NI-PEI and NI-PEI/PEI mixtures were blended with an epoxy resin (MY0510) which was cured with 3,3′-diaminodiphenolsulfone. The morphology and fracture behaviour of these blends were examined by dynamic mechanical thermal analysis and by a three-point bending fracture test. A two-phase morphology exists with substantial toughening occurring at PEI and NI-PEI concentrations of 5 and 10 wt%.

(Keywords: blends; miscibility; fracture behaviour)

INTRODUCTION

In recent years, some significant work[1,2] on polyfunctional epoxy resin modification has been undertaken to improve toughness in order to meet demanding structural applications. To retain the advantages of the high glass transition temperature of the epoxy resin, a polyetherimide (PEI: Ultem 1000) was chosen as a modifier for the epoxy resin (MY0510). The desired morphology for the toughening of thermosetting polymers is a two-phase morphology with strong interactions at the interface[3]. In this incompatible blend[2], the interaction between the matrix and the occluded phases (PEI) could be strengthened by appropriate chemical modification of the PEI. Complete miscibility is not desired[4,5].

This paper reports on the nitration of the polyetherimide (NI-PEI) which was then carefully characterized prior to being blended with the trifunctional epoxy resin.

EXPERIMENTAL

Materials

Both the MY0510, a trifunctional epoxy resin (triglycidylparaaminophenol), and the hardener, 3,3′-diaminodiphenolsulfone (3,3′-DDS), used in this work were kindly donated by Ciba Geigy. The PEI (Ultem 1000) was provided by General Electric. See *Figure 1* for the molecular formulae.

Modification of PEI

A 25 ml sample of a 20% nitric acid solution was poured into a 500 ml round-bottomed flask and then 12.5 ml of 98% sulfuric acid was added to the flask, now in a cold water bath. When the temperature of the mixed acids reached 20°C, a solution of 5 g of PEI in dichloromethane was added to the flask, with stirring, over a 20 min period. The reaction solution was then poured slowly into a large excess of distilled water. Water washing was repeated several times and was followed by repeated ethanol washes. The sample was redissolved in dichloromethane and reprecipitated with ethanol to remove any residual impurities. It was then dried under vacuum at 80°C for at least 5 h.

Characterization of the modified PEI

The nitrogen contents of the PEI and NI-PEI materials were measured using a Carlo Erba elemental analyser (model 1106).

Nuclear magnetic resonance (n.m.r.) and i.r. spectra were obtained using a Jeol 400 MHz n.m.r. spectrometer in CD_2Cl_2 as solvent, and a Perkin-Elmer 1720-X Fourier transform infra-red spectrometer, respectively.

In order to determine the intrinsic viscosity, $[\eta]$, 0.5 g samples were dissolved in 25 ml of dichloromethane. A 10 ml sample of the solution was placed in an Ubbelohde suspended-level viscometer. Subsequent dilution was obtained by adding known amounts of solvent directly to the viscometer. Flow-time data were treated using both the Huggins[6] and the Kraemer[7] formulae.

Blending procedure

Weighed mixtures of the epoxy resin (MY0510) and of 3,3′-DDS were mixed with PEI or NI-PEI, which was initially dissolved in dichloromethane. Initial degassing

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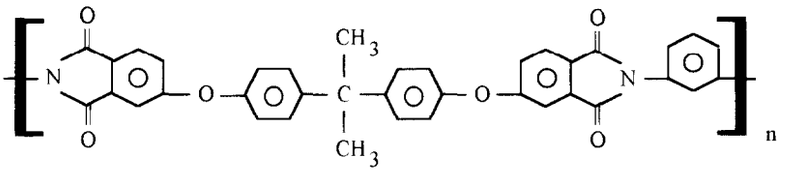
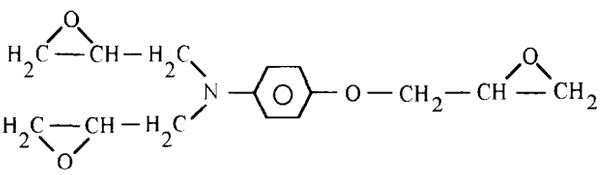
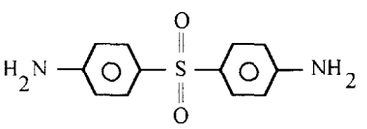


(PEI)



(MY0510)



(3,3'-DDS)

Figure 1 Structural formulae of PEI and the epoxy resin components

and solvent removal was carried out at 80°C in an oil bath for about 30 min. The samples were then poured into a mould (15 cm × 20 cm) which was preheated to 140°C in a vacuum oven where further degassing occurred under vacuum for about 30 min. The samples were then cured at 180°C for 2 h. Post-curing was conducted at 200°C for 10 h. After the cure, or post-cure, the oven was switched off and allowed to cool slowly to room temperature to avoid crack formation.

The samples for mechanical testing were machine-cut into 1 cm wide strips and those for impact testing were machine-notched in the centre of the strips to a depth of about 2 mm. The notches were sharpened by lightly pressing a razor blade into the notch tip to give an overall notch depth of *c.* 2 mm.

Instrumentation

Dynamic mechanical data were obtained using a Polymer Laboratories dynamic mechanical thermal analyser. The samples were run in the single-cantilever bending mode at a frequency of 10 Hz and at a heating rate of 3°C min^{-1}. Glass transition temperatures (T_gs) were taken from the maxima in the tan δ–temperature plots. A Perkin Elmer DSC 7 differential scanning calorimeter was also used to determine the T_gs of the PEI and NI-PEI samples. The heating rate was 20°C min^{-1}.

Fracture data were obtained (20°C) from three-point bending experiments using a modified Nene MC 3000 tensometer. The cross-head speed was 1 mm min^{-1}. See reference 2 for further details.

RESULTS AND DISCUSSION

Characterization of the nitrated polyetherimide

The characterization data are shown in *Table 1*. The results of n.m.r. and i.r. spectroscopies and of the elemental analysis show that the nitration of PEI was effected. Typically, aromatic nitro groups absorb strongly at 1534 cm^{-1} in the i.r. region. This band was found in the i.r. spectrum of the NI-PEI sample (see the shaded peak in *Figure 2b*). By comparing the total signals from the aromatic to aliphatic hydrogens, the n.m.r. spectra proved that, on average, 2.2 hydrogen atoms per repeat unit had been substituted by $-NO_2$ groups. A similar number (1.9) of $-NO_2$ groups per repeat unit was calculated from the elemental analysis results.

Figures 3 and *4* show partial 400 MHz ^{1}H and 100 MHz ^{13}C spectra for PEI (lower trace) and NI-PEI (upper trace). It is clearly seen that residual signals from unmodified repeat units within the NI-PEI material have very low intensities. For example, there are major H

Table 1 Characterization data for the PEI and NI-PEI polymers

Material	PEI	NI-PEI
T_g (°C)[a]	216	231
Content of N (%)[b]	4.68	8.12
Average number of $-NO_2$ groups per repeat unit[b]	0	1.9
Average number of $-NO_2$ groups per repeat unit[c]	0	2.2
$[\eta]$ (ml g^{-1})	0.70	0.33

[a] By differential scanning calorimetry
[b] By elemental analysis
[c] By n.m.r. spectroscopy

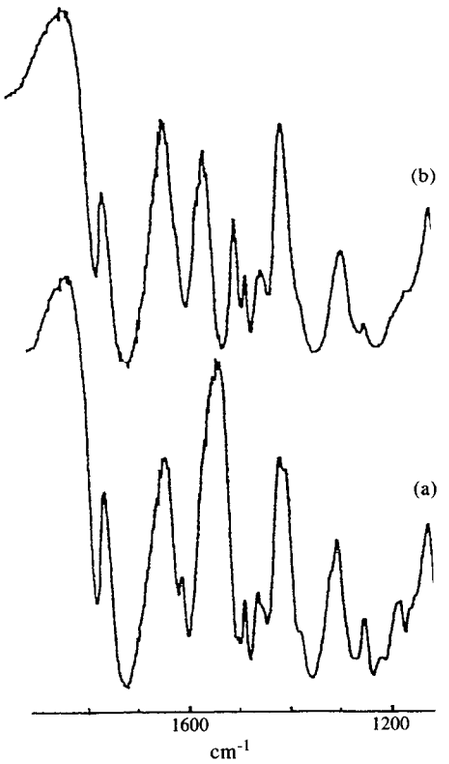


Figure 2 Infra-red spectra of (a) PEI and (b) NI-PEI

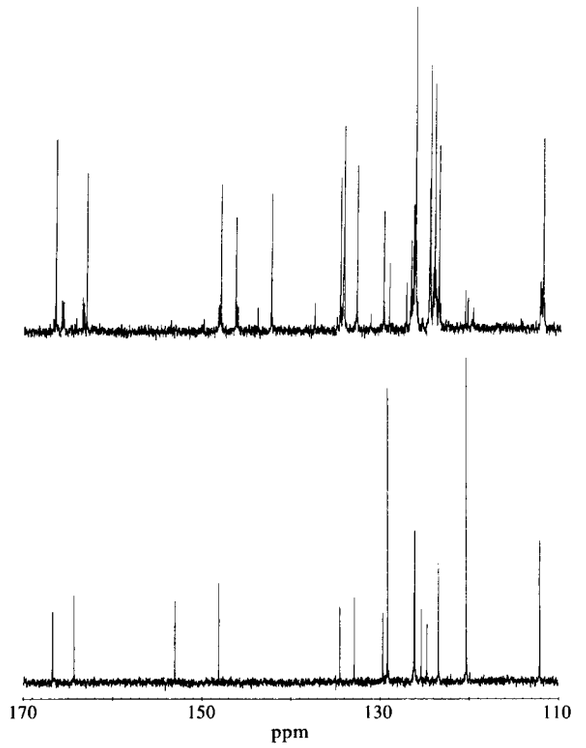


Figure 4 ^{13}C n.m.r. spectra of PEI (lower trace) and NI-PEI (upper trace)

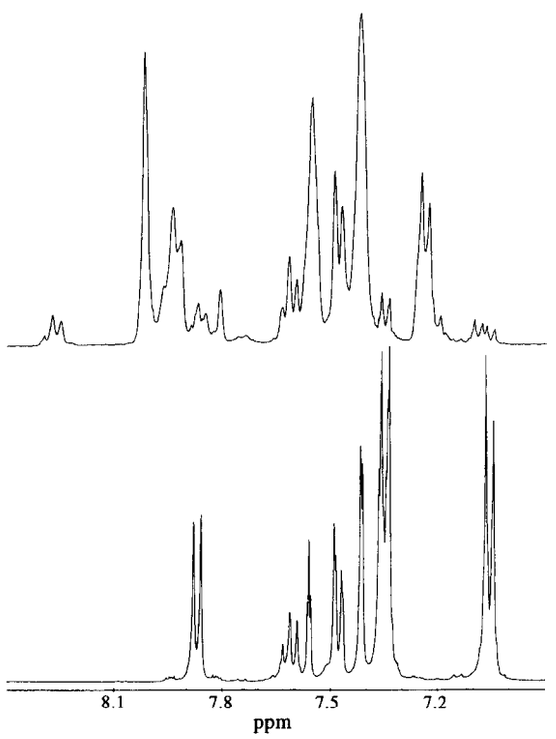


Figure 3 ^{1}H n.m.r. spectra of PEI (lower trace) and NI-PEI (upper trace)

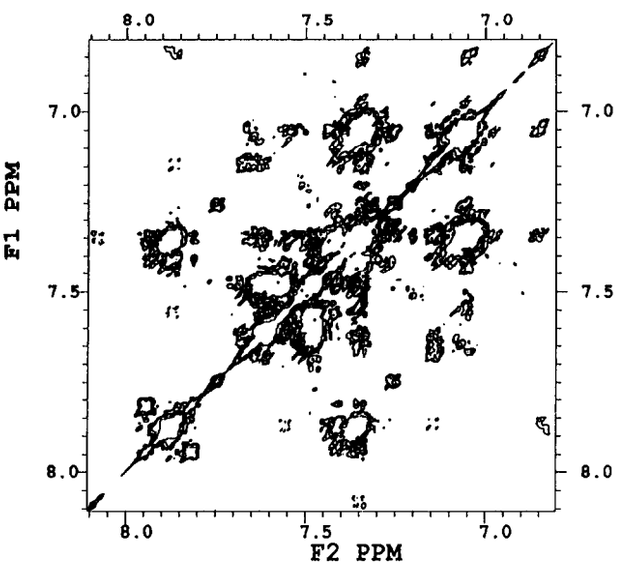


Figure 5 COSY-45 n.m.r. spectrum of PEI

resonances at 7.05 and 7.35 ppm which correspond to the two *para*-substituted polyether aromatic ring systems in PEI. In the upper trace in *Figure 3*, a residual signal from an unsubstituted environment is seen, with a second doublet just downfield which probably represents a repeat unit in which a neighbouring ring has become nitrated. Similarly, the resonances from the three protons in each of the two imide aromatic systems, at *c.* 7.37, 7.42 and 7.87 ppm, are also greatly attenuated; thus the aromatic rings within both of these components are extensively nitrated in NI-PEI.

By contrast, the weak set of responses from the smaller *meta*-substituted linking components, which can be seen at *c.* 7.48, 7.56 and 7.62 ppm, remain essentially unchanged

Table 2 Values of K_{1c} and G_{1c} of the pure epoxy resin and the blends

Composition (wt%)	Treatment	K_{1c} (MN m$^{-3/2}$)	G_{1c} (kJ m^{-2})
0% PEI	Cure	0.89 ± 0.13	0.25 ± 0.07
	Post-cure	0.91 ± 0.12	0.26 ± 0.06
5% PEI	Cure	1.30 ± 0.21	0.55 ± 0.16
	Post-cure	0.80 ± 0.12	0.26 ± 0.06
5% NI-PEI	Cure	1.20 ± 0.17	0.51 ± 0.09
	Post-cure	0.98 ± 0.08	0.31 ± 0.05
10% PEI	Cure	1.89 ± 0.22	1.06 ± 0.26
	Post-cure	1.09 ± 0.04	0.36 ± 0.04
10% NI-PEI	Cure	1.70 ± 0.13	0.86 ± 0.11
	Post-cure	0.99 ± 0.03	0.32 ± 0.02
15% PEI	Cure	1.18 ± 0.10	0.47 ± 0.06
	Post-cure	1.21 ± 0.08	0.49 ± 0.05
15% NI-PEI	Cure	0.94 ± 0.07	0.30 ± 0.04
	Post-cure	0.84 ± 0.12	0.25 ± 0.06
25% PEI	Cure	1.56 ± 0.11	0.78 ± 0.09
	Post-cure	1.55 ± 0.05	0.77 ± 0.04
25% NI-PEI	Cure	0.84 ± 0.02	0.25 ± 0.04
	Post-cure	0.80 ± 0.10	0.24 ± 0.04
25% (75 PEI : 25 NI-PEI)	Cure	1.51 ± 0.04	0.73 ± 0.04
	Post-cure	1.58 ± 0.05	0.82 ± 0.02
25% (25 PEI : 75 NI-PEI)	Cure	1.04 ± 0.07	0.34 ± 0.03
	Post-cure	0.90 ± 0.10	0.30 ± 0.02

upon nitration, suggesting that little substitution has taken place within this third structural moiety.

The ^{13}C spectra (*Figure 4*) confirm these data. In particular, the two dominant signals from the polyether aromatic rings almost disappear upon nitration.

The coupled sets of protons in PEI were readily identified by means of a two-dimensional COSY-45 experiment. Examination of the lower trace in *Figure 3*, together with *Figure 5*, where the COSY-45 data are displayed with contour levels chosen to emphasize minor co-components, illustrates that within the PEI starting material there is not absolute structural homogeneity. Several minor sets of responses are seen, which may be due either to end-group effects or, more probably, to structural variations within the main PEI backbone.

The nitration of PEI may well have been accompanied by some degradation because imide groups are somewhat sensitive to strong inorganic acids. The intrinsic viscosity, [η], of the pure PEI was much higher than that of the modified NI-PEI sample. The introduction of the relatively bulky and polar nitro groups in the NI-PEI will make the backbone even more stiff and rod-like. The T_g of the NI-PEI sample was increased relative to the unmodified PEI by 15°C, as measured by differential scanning calorimetry. Any significant reduction in molecular weight would tend to reduce the T_g. Hence, this rise in T_g is thought to indicate that substantial degradation has not taken place, and that the decrease in [η] on derivatization may be caused by the increased polarity of the NI-PEI resulting in a significant change in nature of the polymer–solvent interactions.

Fracture behaviour

A series of blends containing 5, 10, 15 and 25 wt% of either the PEI or the NI-PEI thermoplastic were prepared. At the 25 wt% level only, two mixed PEI/NI-PEI blends were also prepared.

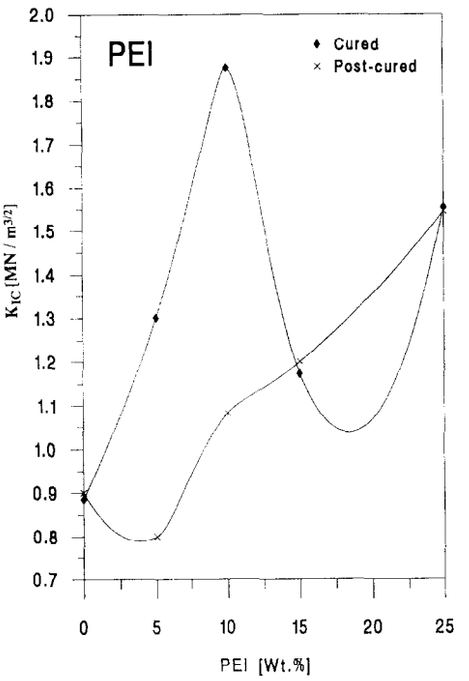


Figure 6 Critical stress intensity factor *versus* PEI concentration for cured and post-cured epoxy resin/PEI blends

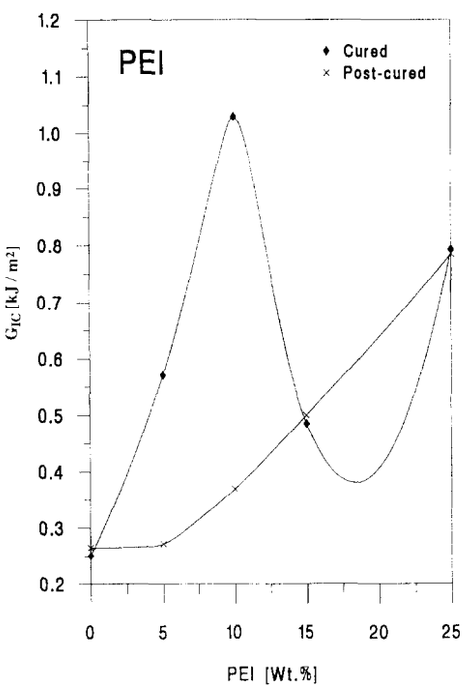


Figure 7 Critical strain energy release rate *versus* PEI concentration for cured and post-cured epoxy resin/PEI blends

Values[1,2] of the critical stress intensity factor, K_{1c}, and the critical strain energy release rate, G_{1c}, were calculated from the three-point bending test data and are listed in *Table 2*. The pure epoxy resin is, of course, brittle, with relatively low K_{1c} and G_{1c} values and post-curing has no significant effect. *Figures 6–9* show more clearly how K_{1c} and G_{1c} vary with composition for the cured and the post-cured materials. A number of trends are evident from these figures.

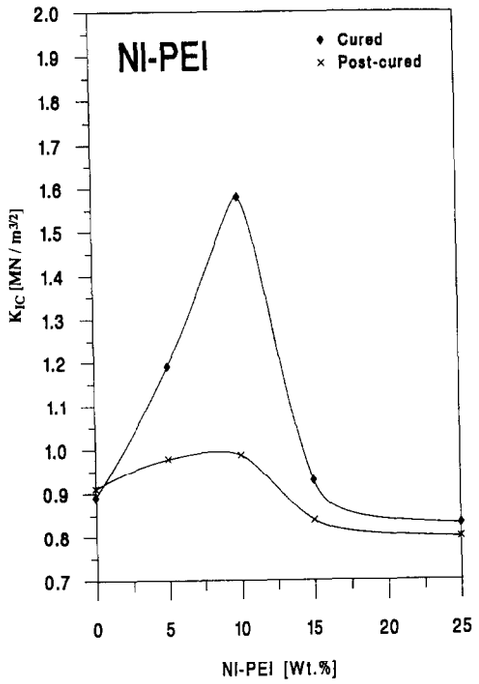


Figure 8 Critical stress intensity factor *versus* NI-PEI concentration for cured and post-cured epoxy resin/NI-PEI blends

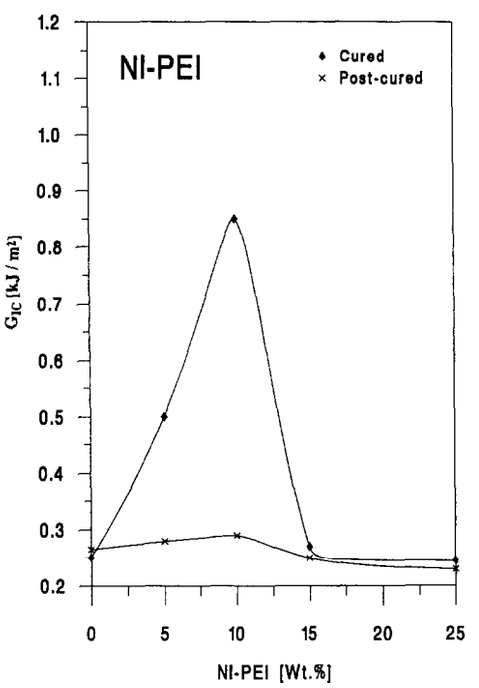


Figure 9 Critical strain energy release rate *versus* NI-PEI concentration for cured and post-cured epoxy resin/NI-PEI blends

The epoxy resin–PEI blends. Both the K_{1c} and G_{1c} values increase essentially linearly up to 10 wt% PEI. This is followed by a dramatic decrease for the 15 wt% PEI sample and then by a rise again for the 25 wt% material. Scanning electron microscopy of the epoxy/PEI blend containing 15 wt% of the thermoplastic shows that the occluded PEI phases were quite large, with some

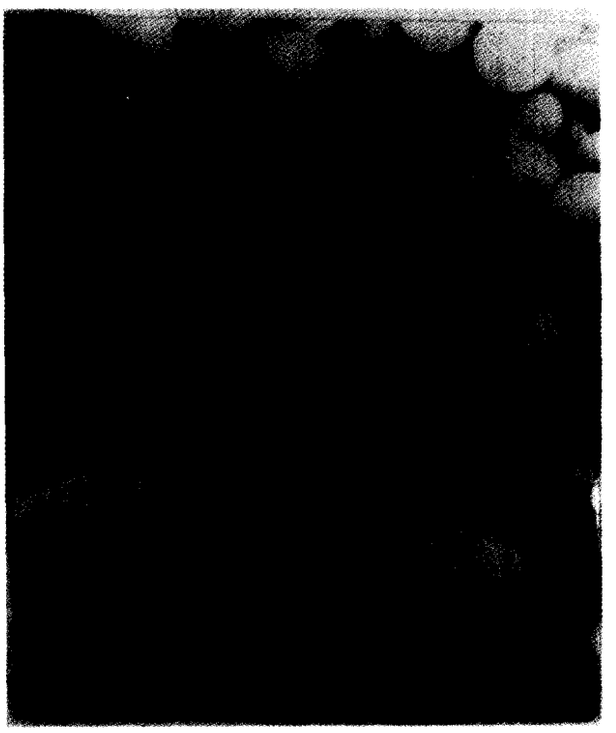


Figure 10 Electron micrograph of the cured epoxy resin containing 15 wt% PEI

Figure 11 Electron micrograph of the cured epoxy resin containing 25 wt% of a mixture of PEI (75%) and NI-PEI (25%)

of these approximately spherical phases having diameters in excess of 10 μm. *Figure 10* shows a scanning electron micrograph of a sulfuric acid-etched fracture surface of a non-post-cured sample. It is believed[8,9] that at this size they are too large to contribute significantly

to toughening of the epoxy matrix. This was not the case at the 5 and 10 wt% levels. The increase again at 25 wt% PEI is believed to arise from incipient phase continuity of the thermoplastic component. This can be seen in *Figure 11*, which shows a blend containing 25 wt% NI-PEI, but is typical also of the pure 25 wt% PEI blend. This figure also tends to indicate that in this epoxy/PEI blend there is not a strong interface between the components.

Except at the higher compositions, where there was no significant effect, post-curing the blends greatly reduced their toughness. The morphology of etched fracture surfaces of the post-cured 15 wt% PEI blend did not differ significantly from the morphology of the sample which had not been post-cured. As post-curing the pure epoxy resin had no measurable effect on the K_{1c} or G_{1c} values, and also did not influence the size of the PEI domains, it was deduced that the relative lack of toughness enhancement in post-cured samples at PEI loadings of up to 10 wt% was the consequence of a weakening of the epoxy–PEI interface.

The epoxy resin/NI-PEI blends. When the PEI is replaced by NI-PEI, the same initial increases in K_{1c} and G_{1c} were observed. Again, there is a very rapid decrease in both of these parameters at the 15 wt% level, but, unlike the PEI case, these values continue to decrease slightly with added NI-PEI. Scanning electron microscopy showed no resolvable phase structure at the magnifications used previously. There was some indication in the micrographs that phases significantly below 1 μm may exist. Clearly, the nitration of PEI has resulted in a significantly more miscible and consequently less toughened system.

This makes it possible that a mixture of PEI and NI-PEI could be used to control both the size of the occluded thermoplastic phases and the strength of the thermoset–thermoplastic interface. As an initial investigation of this possibility, two blends containing an overall 25 wt% of the thermoplastic component were prepared. These two blends contained, firstly, a 75:25 ratio of PEI:NI-PEI, and secondly, a 25:75 PEI:NI-PEI ratio. Comparison of *Figures 11* and *12* shows that very different morphologies arise. With the higher level of NI-PEI, the occluded phases are much smaller and some phase-in-phase morphology exists.

From *Table 2* it is apparent that the higher NI-PEI composition results in markedly lower K_{1c} and G_{1c} values. For the 75:25 PEI:NI-PEI case, these values are, within error, the same as those for the blend containing 25 wt% of PEI alone.

Further studies will be undertaken on the effect of adding less than 25 wt% of the NI-PEI thermoplastic.

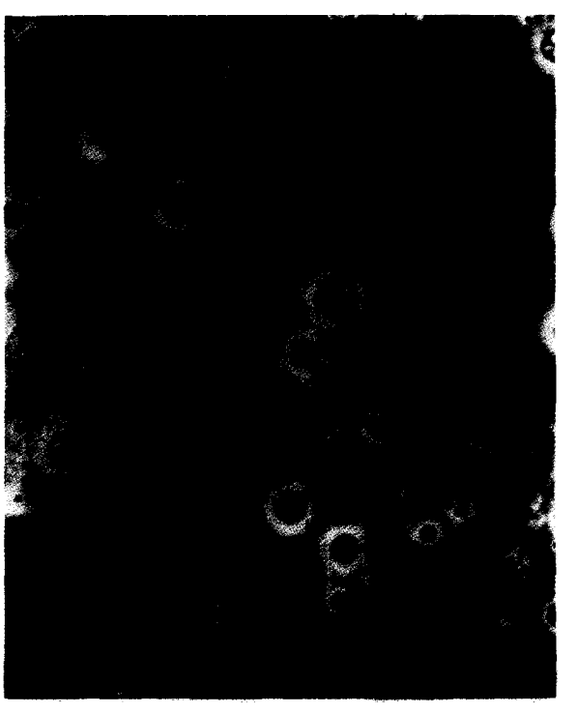


Figure 12 Electron micrograph of the cured epoxy resin containing 25 wt% of a mixture of PEI (25%) and NI-PEI (75%)

Table 3 Glass transition temperatures of the pure epoxy resin and the blends obtained by dynamic mechanical thermal analysis

Sample	Treatment	T_g (°C)
Pure epoxy	Cure	232
	Post-cure	240
5% PEI blend	Cure	229
	Post-cure	236
5% NI-PEI blend	Cure	230
	Post-cure	232
10% PEI blend	Cure	228
	Post-cure	237
25% (75 PEI : 25 NI-PEI) blend	Cure	216
	Post-cure	229
Pure PEI		228
NI-PEI		246

Dynamic mechanical thermal analysis

The T_gs of the pure epoxy resin and the blends are listed in *Table 3*. As the T_gs of the epoxy resin and of the PEI are very similar, this technique will be of limited value as far as unravelling the blend morphologies is concerned. Nonetheless, some useful information was accrued by this method.

Firstly, post-curing the pure epoxy resin did result in both an increase in T_g and a narrowing of the transition region[10] arising from a tighter and more uniform network. Also, nitrating the PEI resulted in an increase of 18°C in the T_g. A 15°C rise, from measurement by d.s.c., was reported in *Table 1*.

For the blends containing 5 and 10 wt% of PEI or NI-PEI, the observed single transition (cured or post-cured) was not much shifted compared to that of the equivalent pure epoxy resin. However, the NI-PEI-containing blends had slightly narrower transitions, which was taken to be indicative of a more miscible system, as already postulated from the electron microscopy studies. With these blends, annealing also caused transition narrowing, as seen for the pure epoxy networks.

For the blend containing 25 wt% of the thermoplastic in which the PEI to NI-PEI ratio was 75:25, the T_gs of the cured material were significantly lower than for the other systems, including the blends. Post-curing raised the T_g to the level of the other materials. This lower value could be the result either of the increased degree of miscibility, or of some of the epoxy resin or 3,3′-DDS

hardener being soluble in the thermoplastic component, resulting in a looser network.

Further studies are required of the effect of adding varying amounts of NI-PEI to the blends showing maximum toughening. There could be significant advantages. Benefits could also accrue in systems in which some, or all, of the nitro groups are reduced to primary amine groups, which are then available to react directly with the MY0510 or other epoxy resins.

CONCLUSIONS

N.m.r. spectroscopy and other evidence showed that the PEI had been nitrated to a considerable extent. Blends of the epoxy resin with PEI showed substantial phase separation, with thermoplastic concentrations up to 10 wt% showing large increases in the critical stress intensity factor and in the critical strain energy release rate. At about 25 wt% of PEI, there was evidence for the PEI beginning to behave as a continuous phase. The nitrated PEI was more compatible with the epoxy resin and consequently the toughening effect was reduced.

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