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Blends of thermoplastic polyimide with epoxy resin

Part II *Mechanical studies*

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Bifunctional epoxy resins have been modified with thermoplastic polyimide in order to improve their toughness. The effects of polyimide content, curing conditions, curing agents, and types of polyimide on the fracture properties have been examined. Relationships between the microstructure of the cured resins and their mechanical properties have also been investigated.

1. Introduction

The inclusion of rubber into epoxy resins in order to improve the fracture toughness has been widely studied [1, 2]. It has been observed that a significant drop in the modulus cannot be avoided in rubber modified materials. Recently, the modification of epoxies with engineering plastics, such as poly (ether sulfone) (PES) [3], poly (ether imide) [4–6], and an amine terminated oligomer of aromatic compounds [7, 8], have been studied and in these cases improved fracture properties have been reported.

One of the authors has previously examined the morphology of thermoplastic polyimide (PI) modified epoxies (Ep) using dynamic mechanical analysis and scanning electron microscopy [9]. The application of these techniques to the study of the matrix resin of carbon fibre reinforced plastics has also been reported [10]. In the previous paper [9], the phase diagram of the epoxy oligomer (diglycidyl ether of bisphenol A; DGEBA)/PI was investigated, and the relationship between the initial miscibility before cure and microstructure of the cured resin was studied. The microstructure in the fractured surfaces of the PI modified Ep varied with the loading levels of PI and the initial cure temperature. The microstructure also changed with variation of the type of PI incorporated into the Ep. Differences in the PI concentrations observed between two separated phases (an epoxy rich phase and a PI rich phase) were effectively determined by phase separation phenomena in the initial cure. The difference in PI concentration between the two phases increased as the initial curing temperature was increased.

In this study, the fracture properties of PI modified epoxies have been studied. The effects of the level of PI concentration, curing agents, curing conditions, and types of PI on the fracture properties are examined.

2. Experimental procedure

The DGEBA was purchased from the Yuka-Shell Epoxy Co. (Epikote 828, Mn = 380). The thermoplastic polyimide (PI) modifiers used were polyetherimide (PEI, Ultem 1000, General Electric, Mn = 12 000, Mw = 30 000), and a series of polysulphoneimides with a molecular weight variation (PSIL, S-63L, Mn = 17 000, Mw = 36 000, and PSIH, S-63H, Mn = 29 000, Mw = 63 000, supplied by the New Japan Chemical Co.). The resin was cured with a stoichiometric ratio of 4,4′-diaminodiphenylmethane (DDM, Tokyo Kasei Kogyo Co.) or 4,4′-diaminodiphenylsulphone (DDS, Tokyo Kasei Kogyo Co.).

The DGEBA and the curing agent mixtures were moulded into glass plates by cast moulding. The preparation of PI modified Ep plates has been described in a previous paper [9]. The resin mixtures loaded with various amounts and/or types of PI were cured under various curing conditions. The PEI and PSIL single composition plates were moulded by press moulding. A PSIH plate could not be moulded because the melt resin was too viscous.

The moulded plates were machined to a size of 40 × 6 × 3 mm. Fracture toughness measurements were performed at 23 °C in the three point bending mode with a span of 24 mm at a crosshead speed of $0.5\,\mathrm{mm\,min^{-1}}$ in compliance with ASTM E399. The fractured surfaces were observed with an Elionixs ESA-2000 scanning electron microscopy (SEM).

3. Results and discussion

3.1. Effect of the PI loading level

Fig. 1 shows the effect of PEI concentration on the fracture toughness (critical values of the stress intensity factor; K_{IC}) measured for the modified Ep samples. Although K_{IC} did not increase for PEI concentrations

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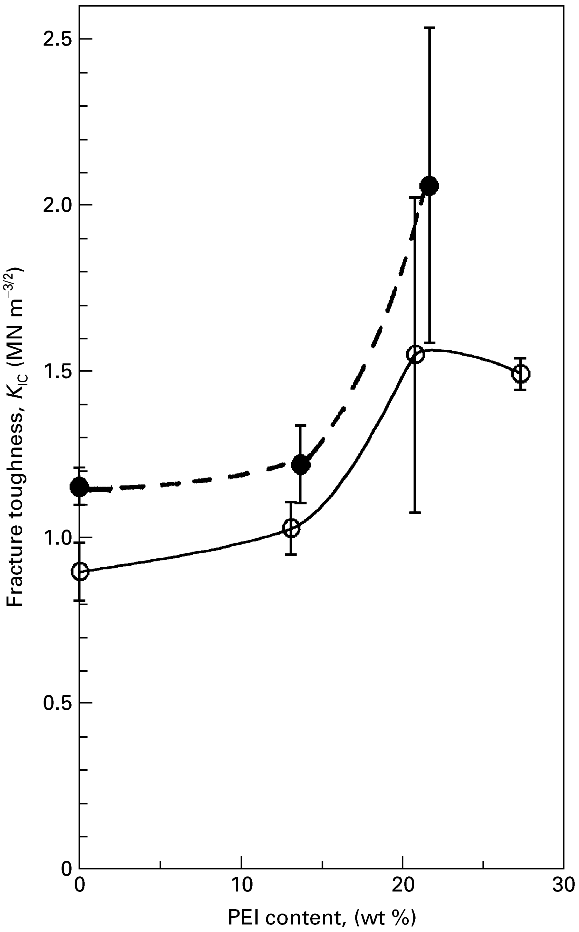

Figure 1 The effect of PEI content and curing agents on the fracture toughness of modified Ep samples; (–○–) DGEBA/DDS/PEI, cured at 160 °C for 6 h and 200 °C for 3 h, (–●–) DGEBA/DDM/PEI, cured at 130 °C for 2 h and 150 °C for 3 h.

less than 14 wt %, it rapidly increased for concentrations greater than 20 wt %. Similar results have been reported for trifunctional epoxy resin/PEI systems [5, 6].

Fig. 2(a–d) shows SEM photographs of the surfaces observed after the fracture tests. SEM photographs of the surfaces fractured at 77 K can be viewed in the previous papers [9, 10].

In both the DDS and DDM cured modified Ep, the amount of ductile drawing was considerably larger for 20 wt % PEI materials (Fig. 2(b and d)) compared to the 14 wt % PEI materials (Fig. 2(a and c)). These results are in good agreement with the results shown in Fig. 1.

From SEM observations on samples etched with dichloromethane, it was ascertained that the black region was an Ep rich phase, whilst the white region was a PI rich phase. In Fig. 2a, both a continuous Ep matrix region (with dispersed PEI domains) and a phase inverted region (PEI matrix and Ep connected globules) can be observed. In Fig. 2c, PEI domains were present in the Ep matrix whilst in Fig. 2(b and d) a globular Ep rich phase was present in the PEI matrix.

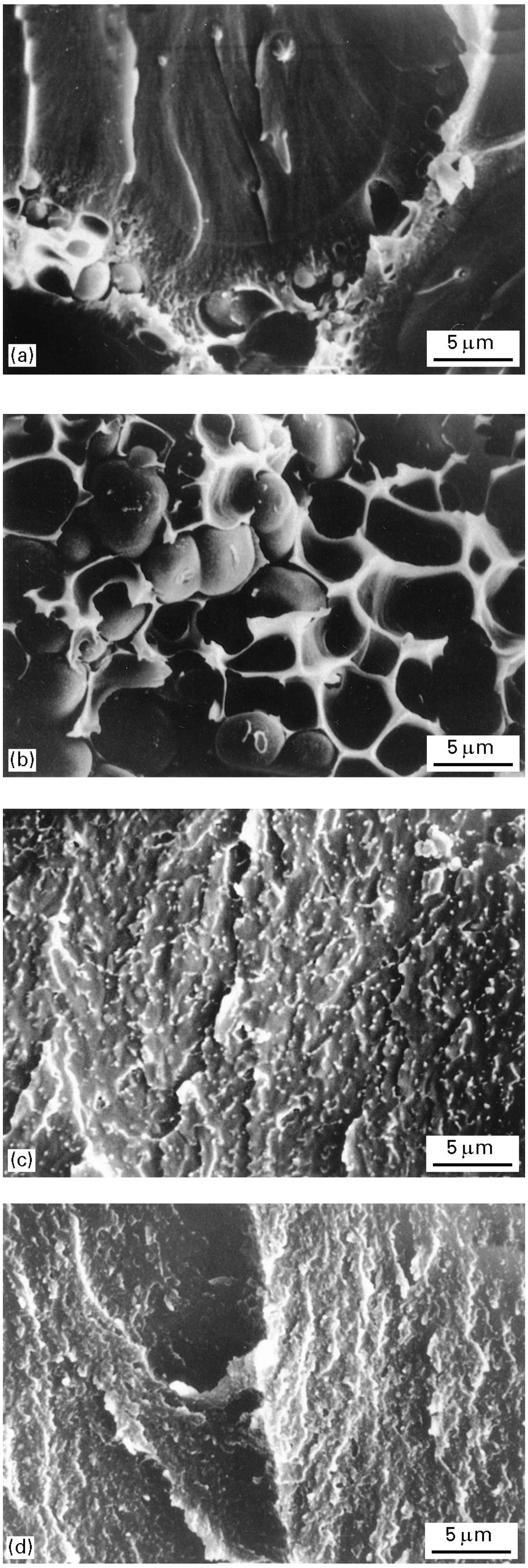

Figure 2 The effect of PEI content and curing agents observed on SEM micrographs taken after the toughness tests. (a) DGEBA/DDS/PEI 14 wt %, (b) DGEBA/DDS/PEI 20 wt %, (c) DGEBA/DDM/PEI 14 wt %, (d) DGEBA/DDM/PEI 20 wt %., curing conditions; (a) and (b), cured at 160 °C for 6 h and 200 °C for 3 h, (c) and (d), cured at 130 °C for 2 h and 150 °C for 3 h.

In the previous study [9], it was shown that for PI modified Ep the phase inversion took place at *circa* 14–20 wt % PI. The fractured surfaces of the 7 wt % PI materials consisted of a continuous Ep matrix with dispersed PI domains. The fracture surfaces of the completely phase inverted samples (loaded with 27 wt % PI) consisted of epoxy connected globules wrapped in layers of the PI rich matrix. The phase structures of the 14–20 wt % PI materials show an intermediate behaviour between those of the 7 and

27 wt % PI materials. The curing conditions, curing agents and the type of PI used all affect the intermediate structures and the composition at which the phase inversion occurs. In Fig. 2(a–d) the phase inversion occurs at *circa* 14 wt % PEI.

An increase in the PEI concentration may also contribute to an increase in the area or thickness of the PEI rich phase. However, any large increases observed in the 14–20 wt % PEI samples should be attributed to the phase inversion.

3.2. Effect of the curing agents

In Fig. 1, it is clear that the K_{IC} values of the DDM cured samples were larger as compared to those of the DDS cured samples for all of the tested PEI concentrations. For the DDS cured samples, the ductile drawing of the PEI rich matrix is presented in Fig. 2(a and b), however, it is not clear if any deformation of the Ep rich globules occured. For DDM cured samples, ductile drawing seems to take place over a larger area as compared to the DDS cured samples. The results in Fig. 2(a–d) were in good agreement with the results in Fig. 1.

When the content of a constituent polymer in a polymer blend varies, it is assumed that both the toughness and phase structure will change. Therefore, it is difficult to decide which factor is the decisive one for toughening.

As can be seen in Fig. 1 (PEI = 0 wt %), the toughness of the DDM cured Ep was larger than that of the DDS cured Ep.

The Ep rich globules in the DDM cured blend sample (Fig. 2d) were smaller as compared with those in the DDS cured sample (Fig. 2b). It has been proposed for the Ep/PES system that the phase structure can be controlled by the relative progress of the competing phenomena of the phase separation and curing reaction [11]. The size of the Ep rich globules is related to the reactivity and solubility of the curing agents [12]. The reactivity of DDM with DGEBA is in general larger than that of DDS. The phase structure should be suppressed at an earlier stage of phase separation for a DDM cured resin compared to that of a DDS cured resin.

We were unable to isolate the dominant factor that produced the larger toughness values in DDM cured samples, since we did not have enough experimental results.

3.3. Effect of the cure conditions

Fig. 3 shows the results of fracture toughness tests conducted on various samples, that reflect the effects of cure conditions and type of PI used. When the PI was not added, K_{IC} hardly varied and was independent of the initial cure temperature. On the other hand, for the 20 wt % PI added samples, the K_{IC} values increased with an increase in the initial curing temperature.

Fig. 4(a–f) shows SEM photographs of the fracture surfaces observed for the samples in Fig. 3. When the groups of photographs (Figs. 2b and 4(a and b), Fig. 4(c and d) and Fig. 4(e and f) are compared, it is apparent that the deformation area in the fracture surfaces increased with an increase in the initial cure temperature.

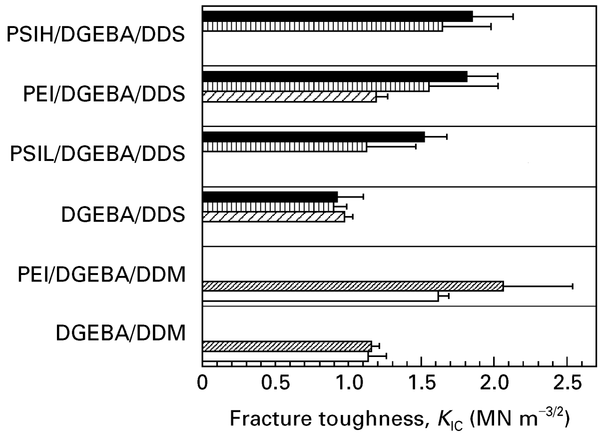

Figure 3 The effect of curing conditions and PI type used on the fracture toughness of modified Ep samples. Curing conditions; (☐) 95 °C 2 h and 150 °C 3 h, (▨) 130 °C 2 h and 150 °C 3 h, (⧄) 130 °C 12 h and 200 °C 3 h, (▥) 160 °C 6 h and 200 °C 3 h and (■) 200 °C 6 h.

In our previous paper [9], it was concluded from the results of dynamic mechanical measurements that the difference in concentration of PI in the two separated phases was effectively determined in the initial phase separation. The concentration difference between the two phases increased (i.e., PI concentration increased in the PI rich phase and decreased in the Ep rich phase) with the initial curing temperature.

It could be considered that the thickness, area and/or toughness of the PI rich matrix could be extended by increasing the PI concentration. In Fig. 4(a–f), it is not clear if the thickness or area of the PI rich matrix increased with the cure temperature. On the other hand, the area of the PI matrix is decreased in Fig. 4(b and d) as compared to Fig. 4(a and c). In this case, the PI may be concentrated into the PI rich matrix and thus the area of the PI rich phase decreases. From Fig. 4(b and d), it can be stated that full phase inversion in the fracture surface is not necessary, however a suitable PI concentration is required for an increase in the toughness.

From these results, the increase in the toughness with initial curing temperature is related to the increase of PI concentration in the PI rich phase.

The Ep rich domain size increased with the initial cure temperature in the PEI and PSIL added samples (Figs 2b and 4(a and b) and Fig. 4(c and d)). However, the domain size decreased slightly in the PSIH added samples (Fig. 4(e and f)). The Ep concentration in the Ep rich phase should increase with the initial curing temperature. An increased Ep concentration may affect the Ep domain size. However, as described above the phase structure should be controlled by the relative progress of the competing phenomena of the phase separation and curing reaction therefore some properties of the resin mixture, such as miscibility and viscosity, should influence the phase structure. Whether or not the Ep domain size affects the toughness is currently not clear.

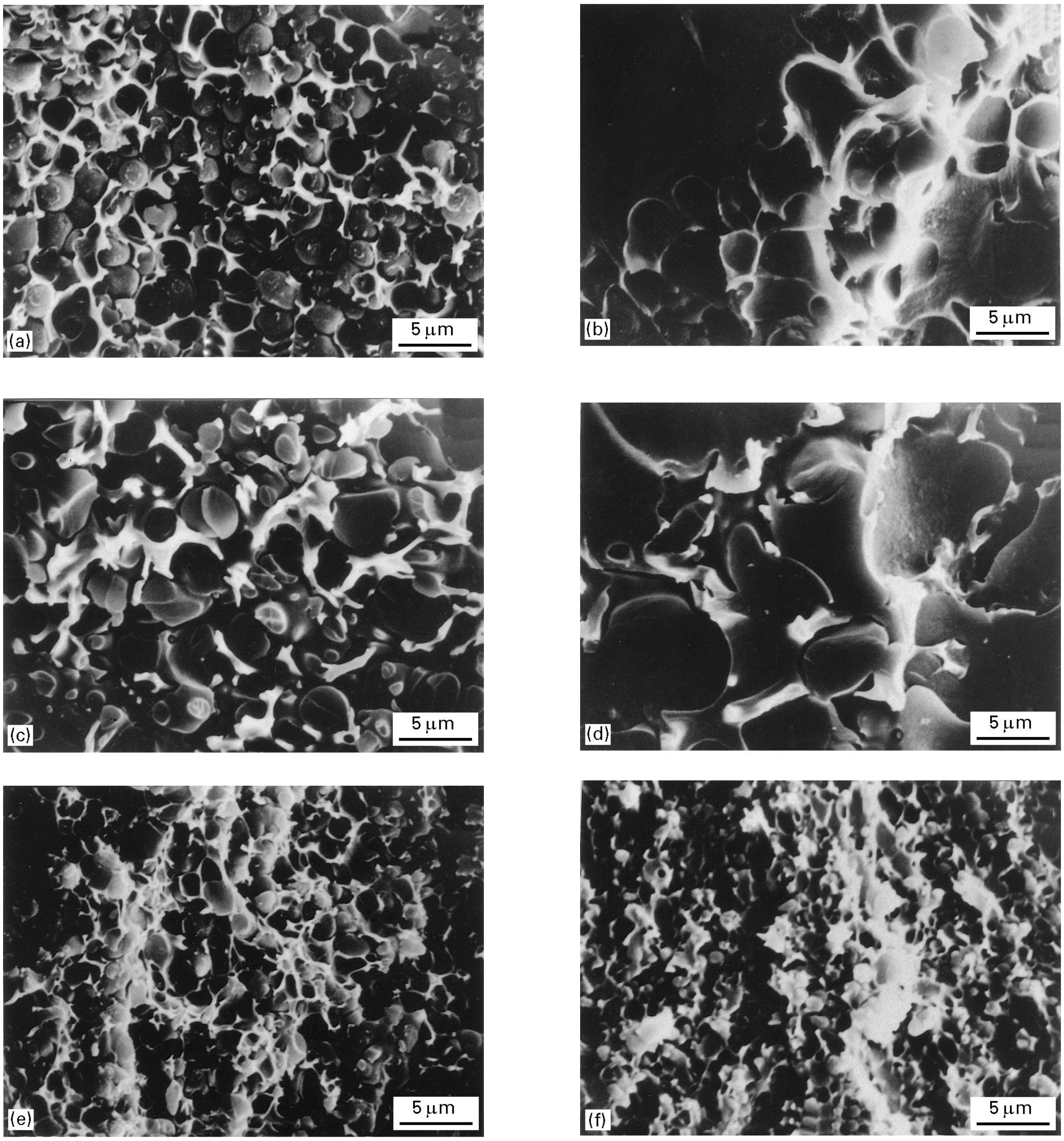

Figure 4 Effect is of curing conditions and type of PI used shown on SEM micrographs taken after the toughness tests. (a) DGEBA/DDS/PEI 20 wt % cured at 130 °C 12 h and 200 °C 3 h, (b) DGEBA/DDS/PEI 20 wt % cured at 200 °C 6 h, (c) DGEBA/DDS/PSIL 20 wt % cured at 160 °C 6 h and 200 °C 3 h, (d) DGEBA/DDS/PSIL 20 wt % cured at 200 °C 6 h, (e) DGEBA/DDS/PSIH 20 wt % cured at 160 °C 6 h and 200 °C 3 h and (f) DGEBA/DDS/PSIH 20 wt % cured at 200 °C 6 h.

3.4. Effect of the PI type used

When the results in Fig. 3 were compared between the different PI used for samples cured under the same conditions the K_{IC} values were in the order; PSIH $\geqslant$ PEI $>$ PSIL.

As previously discussed, in the case where one component in a polymer blend is varied, it is difficult to determine the factor that determines the toughening.

The toughness of the constituent PI were measured. The K_{IC} values measured for single component PEI and PSIL were (3.71 $\pm$ 0.08) and (1.99 $\pm$ 0.28) $\mathrm{MN\,m^{-3/2}}$, respectively.

The phase structure should be affected by the miscibility of the component polymers. As shown in our previous paper [9], the area of the miscible region in the phase diagrams was in the order; DGEBA/PSIL $>$ DGEBA/PSIH $>$ DGEBA/PEI.

A comparison of the grouped figures of Figs 2b and Fig. 4(c and e) and Fig. 4(b, d and f), shows that the phase structure varied with the type of PI used. In Fig. 4(c and d), the Ep rich domains were not globular and the separated two phases appeared to be co-continuous. This morphology in PSIL modified Ep is related to the large miscibility of PSIL/DGEBA [9].

The smallest domain size of the Ep rich phase in fractured PSIH/DGEBA/DDS (Fig. 4(e and f) was observed for materials loaded with 20 wt % modifier. A high molecular weight modifier with a high viscosity may serve as a compound for the formation of PI rich areas, resulting in small Ep domains.

Both the toughness of the component polymer and the phase structure, should help to toughen modified Ep.

4. Conclusion

The fracture properties of PI modified epoxies have been studied. Although the fracture toughness, K_{IC} increased in systems containing more than 20 wt % PEI, no improvement was noted for systems containing less than 14 wt % PEI. In the 20 wt % PI containing samples, the K_{IC} values increased with an increase in the initial curing temperature. In a previous paper [9], it was concluded that the concentration difference between the two separated phases increased with the initial curing temperature. The increase in toughness for the 20 wt % PI containing samples was ascribed to an increase in the PI concentration in the PI rich phase.

The K_{IC} values of the DDM cured samples were larger than those of the DDS cured samples for all the tested PEI contents. Comparing the toughness results for 20 wt % PI added samples cured under the same condition, the K_{IC} values are in the order; PSIH $\geqslant$ PEI $>$ PSIL. In the case where a constituent polymer in a polymer blend is varied, both the toughness of the component and the phase structure are changed. Both these factors should contribute to the toughness of the modified Ep.

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