

Thermoplastic-toughened epoxy polymers

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The microstructure and properties of two epoxy-resin systems which have been modified with varying amounts of a thermoplastic to improve the toughness of the thermosetting epoxy polymers, have been studied. The curing agent was 4,4'-diaminodiphenylsulphone and the thermoplastic was a reactively terminated poly(ether sulphone) copolymer. Different microstructures were found to occur as the concentration of the thermoplastic component was steadily increased. In particular, the relationships between the microstructures and values of stress-intensity factor, K_{Ic} , and fracture energy, G_{Ic} , were explored.

1. Introduction

When cured, thermosetting epoxy polymers typically possess a high cross-link density. This property leads to such materials exhibiting good thermal stability, relatively high modulus and creep resistance and excellent adhesion properties and this combination of properties has led to their widespread use as matrices for fibre-composite materials. Unfortunately, the high cross-link density also leads to a low ductility and a poor fracture toughness being exhibited by the epoxy polymers.

In order to improve the fracture resistance of thermosetting epoxy polymers, a most successful route is to form a blend with a low molecular-weight rubber, where the rubber undergoes phase separation upon curing the epoxy-rubber blend [1–6]. The rubber-toughened epoxy often possesses outstanding fracture properties, and this technology has been widely exploited in the area of engineering adhesives [7]. However, the presence of the rubber phase does somewhat decrease the modulus and thermal stability of the material, and increase the tendency for water absorption with an accompanying loss of properties at elevated temperatures. Whilst for adhesive applications such decreases in modulus and temperature resistance are usually of no significance, in fibre-composite applications such effects can often lead in unacceptable decreases in the properties of the fibre-composite.

Therefore, an alternative approach to toughening epoxy materials which are intended to be used as matrices for fibre-composites has been reported [8–18] in the literature. This approach is to blend the epoxy resin with a thermoplastic that has a high glass transition temperature, good thermal stability and a low propensity to absorb moisture. Thermoplastics, such as poly(ether sulphone) [8, 9, 12, 14, 15, 18] and poly(ether imides) [13, 16, 18], have been blended with epoxy resins, with the formulation of the cured epoxy polymer typically designed to lead to a relatively high

glass-transition temperature. However, unlike the rubber-toughened epoxy polymers, there is little known about the detailed relationships between the microstructure and toughness of thermoplastic-toughened epoxy polymers. Therefore, the present work was concerned with studying the microstructure and properties of two epoxy-resin systems which have been modified with varying amounts of a reactively terminated poly(ether sulphone) copolymer. In particular, the relationships between the microstructures and values of stress intensity factor, K_{Ic} , and fracture energy, G_{Ic} , have been explored.

2. Experimental procedure

2.1. Materials and their preparation

Two epoxy resins were employed in the current studies. They were (i) the triglycidyl aminophenol epoxy ("MY0510", Ciba Geigy plc, UK) and (ii) a difunctional epoxy which was the diglycidyl ether of bisphenol F ("PY306", Ciba Geigy plc, UK). The curing agent was 4,4'-diaminodiphenylsulphone ("HT976", Ciba Geigy plc, UK). The thermoplastic was a reactively terminated poly(ether sulphone) copolymer (ICI plc, UK) and the concentration of the added thermoplastic was varied between 0 and about 140 parts per hundred (p.h.r.) of epoxy resin(s). In these studies both a single-component epoxy-resin system and a two-component epoxy-resin system were examined. The former consisted of the triglycidylaminophenol epoxy cured with 4,4'-diaminodiphenylsulphone, and containing various concentrations of the reactively terminated poly(ether sulphone) copolymer. The ratio of epoxy resin to curing agent was 1.84:1 by weight. The latter, two-component epoxy system, consisted of the triglycidyl aminophenol epoxy and the diglycidyl ether of bisphenol F epoxy. The ratio of the two resins was 1:1.05 and the curing agent was again 4,4'-diaminodiphenylsulphone. The ratio of the epoxy resins to curing agent was 2.6:1 by weight.

The granules of the reactively terminated poly(ether sulphone) copolymer were dissolved in a methylene chloride/methanol (95/5 by volume) to which the epoxy resin (or mixture of epoxy resins) and the 4,4'-diaminodiphenylsulphone curing agent were added. The mixture was then cast into an open steel mould, which had been preheated at 145 °C, and degassed for 30 min at 145 °C in a vacuum oven, under vacuum. The mould was then transferred to an oven at 180 °C and the mould was levelled. The materials were then cured by heating the single-component epoxy-resin system for 1 h at 180 °C and the two-component epoxy system for 3 h at 180 °C. In both cases, after these cure times the oven was switched off and the mould, containing the cured sheet of thermoplastic-toughened epoxy, was allowed to cool slowly.

2.2. Material characterization

To ascertain the microstructures of the thermoplastic-toughened epoxy materials, specimens were polished and etched, as described below. A thin layer of platinum, having a fine grain size, was then evaporated on to the etched surfaces and the microstructures were examined using a "Hitachi S520" or "S800" scanning electron microscope. The micrographs were analysed, using an image analyser, to determine the size and volume fraction of any phase-separated microstructures. The etching method used was firstly to prepare a solution of a small quantity of potassium permanganate (0.05–0.3 g) in 10 ml acid mixture (5:2:2 by volume of concentrated sulphuric acid: concentrated phosphoric acid: distilled water) using an ultrasonic agitation bath. This solution was then cooled to 2–5 °C, and the sample was etched in the stirred solution for 2 min. The specimen was then removed and rinsed very thoroughly using an ultrasonic agitation bath. It was first rinsed in 10:1 concentrated sulphuric acid: distilled water, and this was repeated three to four times. The specimen was then rinsed in 100 volume hydrogen peroxide, distilled water, and finally ethanol.

The microstructure was also studied using dynamic mechanical thermal analysis (equipment supplied by "Polymer Laboratories"). Specimens, in the form of bars 50 mm × 10 mm and between 2.5 and 3.5 mm thick, were tested in a double-cantilever beam mode over the temperature range –85–285 °C and at frequencies of 1–90 Hz. The storage modulus, loss modulus and loss factor, $\tan \delta$, were deduced as a function of temperature for a given frequency.

2.3. Mechanical properties

The modulus of the materials was determined using three-point bending tests, according to ASTM Standard D790 M-86. The rest rate employed was 0.5 mm min⁻¹.

The stress-intensity factor at the onset of crack growth, K_{Ic} , was determined using compact tension test specimens, which were 20 mm × 20 mm × 3.5 mm in size. The specimens were firstly pre-cracked by cutting a crack using a small hacksaw,

followed by gently tapping a razor blade into the cut so as to grow a natural crack ahead of the razor blade. The tests were conducted at a rate of 0.5 mm min⁻¹. The test results all met the criteria [19] for assuming that a linear-elastic fracture-mechanics could be adopted, and the value of K_{Ic} is therefore given by

$$K_{Ic} = Y \frac{P_c}{BW^{1/2}} \quad (1)$$

where P_c is the load for the onset of crack growth, B is the thickness, W is the width and Y is a geometry factor given by

$$Y = \frac{[2 + (a/W)]}{[1 - (a/W)]^{3/2}} \left[0.886 + 4.64 \left(\frac{a}{W} \right) - 13.32 \left(\frac{a}{W} \right)^2 + 14.72 \left(\frac{a}{W} \right)^3 - 5.6 \left(\frac{a}{W} \right)^4 \right] \quad (2)$$

Now the value of the fracture energy, G_{Ic} , is related to K_{Ic} by the expression

$$G_{Ic} = \frac{K_{Ic}^2}{E} (1 - \nu^2) \quad (3)$$

where E is the modulus (from the three-point bend tests and taken at the corresponding rate of test) and ν is the Poisson's ratio taken to be 0.35.

3. Results and discussion

3.1. Single-component epoxy-resin system

This material consisted of the triglycidylaminophenol epoxy cured with 4,4'-diaminodiphenylsulphone and containing various concentrations of the reactively terminated poly(ether sulphone) copolymer.

3.1.1. Microstructures of the polymers

Scanning electron micrographs of specimens of the thermoplastic-modified epoxies containing various concentrations of the reactively terminated poly(ether sulphone) copolymer are shown in Fig. 1. The specimens were etched as described above prior to examination using the electron microscope, and the epoxy-rich phase has been preferentially etched. The poly(ether sulphone) copolymer was found to be soluble in the epoxy up to concentrations of about 8 p.h.r. Therefore, until this concentration of poly(ether sulphone) copolymer was exceeded a single-phase microstructure was formed. At concentrations of more than 8 p.h.r. poly(ether sulphone) copolymer, a second phase, rich in the thermoplastic copolymer, was observed, as shown in Fig. 1a and, as the amount of the poly(ether sulphone) copolymer was increased, epoxy-rich occlusions were observed to form within these second-phase particles. Thus, the second-phase particles also possessed a complex morphology. The diameter of these thermoplastic-rich particles was about 0.2–0.4 μm, the larger particle size being associated with the higher concentrations of added thermoplastic. As further poly(ether sulphone) copolymer was added, the second-phase particles became larger and elongated to form ribbons, see

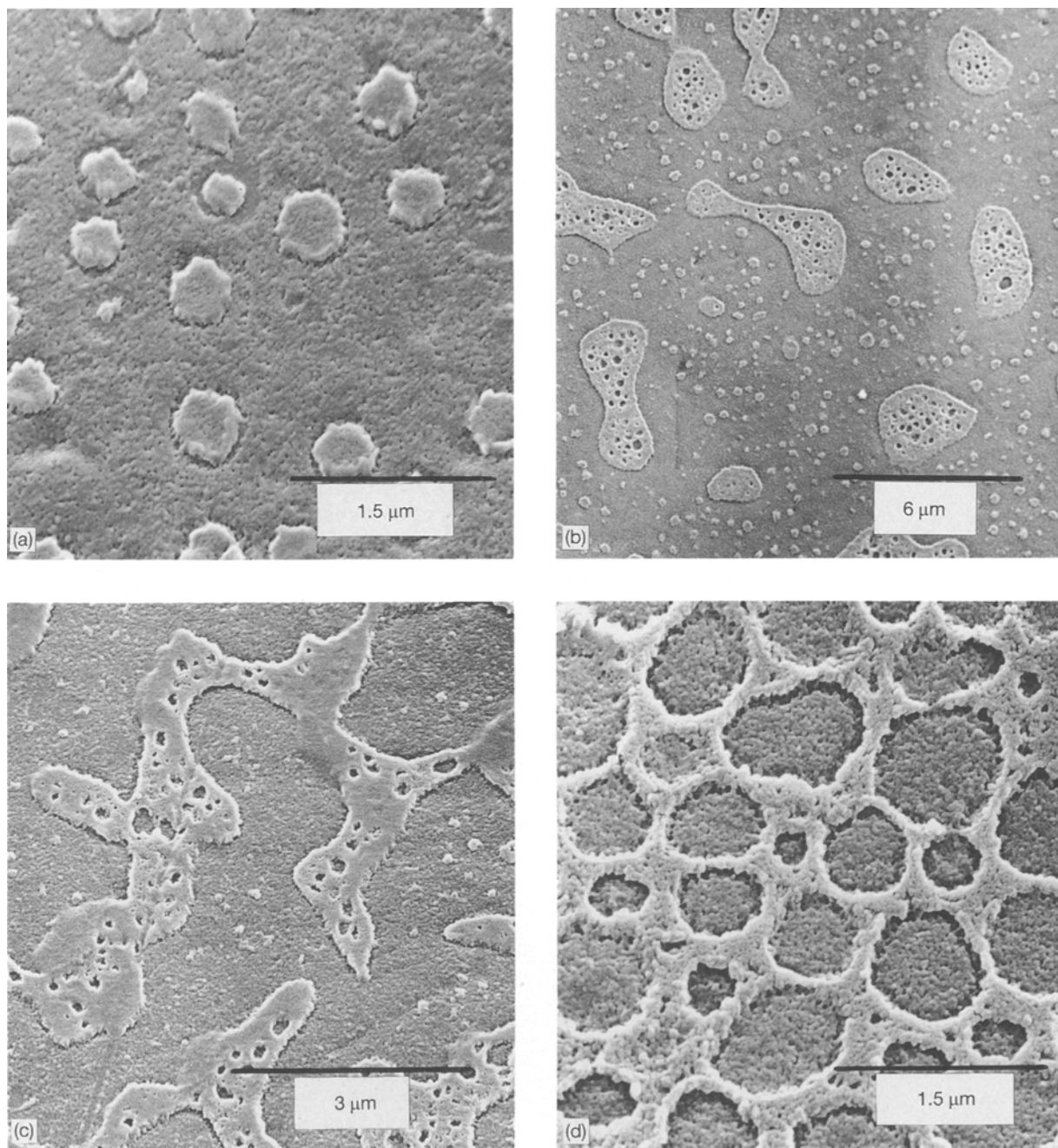


Figure 1 Microstructures of the single-component epoxy-resin system. (a) Particulate microstructure – second phase of thermoplastic-rich particles in continuous epoxy-rich matrix. (b) Particulate and co-continuous microstructures. (c) Co-continuous microstructure – where both the thermoplastic-rich and the epoxy-rich phases are continuous in nature. (d) Phase-inverted microstructure – second phase of epoxy-rich particles in a continuous thermoplastic-rich phase.

Fig. 1b. At a concentration of about 52 p.h.r. poly(ether sulphone) copolymer, it appeared that the thermoplastic-rich phase become co-continuous in nature, as shown in Fig. 1c. These co-continuous ribbons had a typical width of about 0.5–2 μm . Finally, when the blends contained more than 83 p.h.r. poly(ether sulphone) copolymer a phase-inverted microstructure was formed which consisted of a second phase of epoxy-rich particles in a continuous thermoplastic-rich phase. The epoxy-rich particles were approximately 0.1–1.5 μm diameter.

Analysis of the scanning electron micrographs revealed that the volume fraction of the thermoplastic-rich phase increases steadily with increasing concen-

tration of added thermoplastic from the point of initial phase separation (at about 8 p.h.r. added thermoplastic), as may be seen from Fig. 2.

The microstructures of the various blends were also investigated using dynamic mechanical thermal analysis. The temperature of the $\tan \delta$ peaks for the epoxy-rich and thermoplastic-rich phases are shown in Fig. 3 as a function of the concentration of the poly(ether sulphone) copolymer. These peaks represent the glass transition temperatures, T_g , of the two phases. There are several interesting points. Firstly, below 8 p.h.r. added thermoplastic there is no $\tan \delta$ peak for the thermoplastic-rich phase, because phase separation does not occur. Secondly, the initial decline

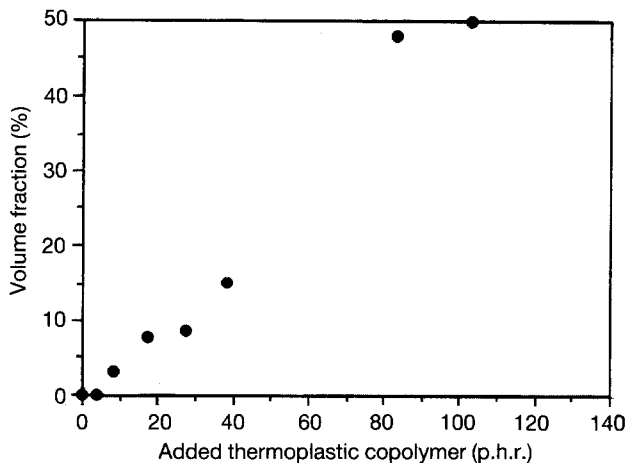


Figure 2 Volume fraction of the thermoplastic-rich phase as a function of added thermoplastic poly(ether sulphone) copolymer concentration. (Single-component epoxy-resin system.)

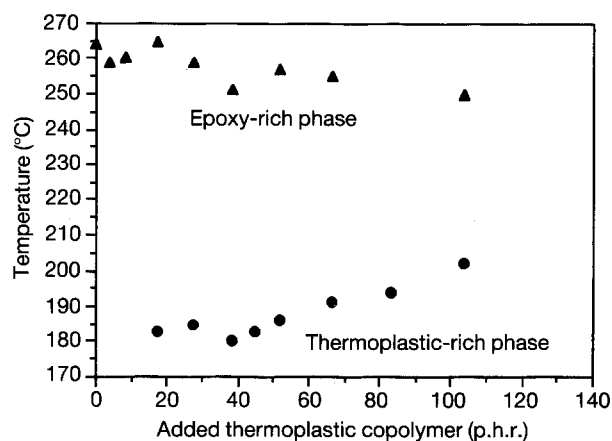


Figure 3 Temperature of the $\tan \delta$ peak (α -transition) for the thermoplastic-rich and the epoxy-rich phases as a function of added thermoplastic poly(ether sulphone) copolymer concentration. (Single-component epoxy-resin system.)

in the T_g for the thermoplastic-epoxy single-phase material is due to the presence of the soluble thermoplastic lowering the T_g of the epoxy polymer. The T_g of the cured epoxy polymer, at 1 Hz, is 264 °C whilst that of the poly(ether sulphone) copolymer is estimated to be about 185–190 °C. (It is not possible to obtain moulded samples for dynamic mechanical thermal analysis, as the poly(ether sulphone) copolymer is too brittle to mould as a result of its low molecular weight ($M_n \approx 10\,000$). However, the T_g may be obtained from differential scanning calorimetry.) Thirdly, at concentrations of more than 8 p.h.r. the added thermoplastic phase-separates to give a thermoplastic-rich phase, and the T_g of the epoxy-rich phase initially recovers to 264 °C but then steadily declines. This steady decline is attributed to the presence of thermoplastic dissolved in the epoxy-rich phase, with the concentration of such dissolved thermoplastic steadily increasing as the total amount of added thermoplastic copolymer is increased. The decrease in T_g suggests that at an added concentration of 100 p.h.r. thermoplastic, when a phase-inverted microstructure is observed (see

Fig. 1d), the epoxy-rich particulate phase contains about 17.5% dissolved thermoplastic. Finally, the steady increase in the T_g of the thermoplastic-rich phase (once phase separation of the thermoplastic copolymer) reveals the presence of dissolved epoxy in this phase; with the amount of epoxy steadily increasing until, at an added concentration of 100 p.h.r. thermoplastic, the continuous thermoplastic-rich phase is estimated to contain about 40% dissolved epoxy.

Thus, a series of different microstructures is produced as the concentration of the reactively terminated poly(ether sulphone) copolymer is increased and these, in turn, can be seen to influence strongly the thermal characteristics of these materials.

3.1.2. Modulus measurements

The flexural modulus, E , of the materials was measured as a function of the concentration of added thermoplastic and the results are shown in Fig. 4. There is an initial rapid decrease in the value of E associated with the low concentrations of added thermoplastic being dissolved in the epoxy, but once phase separation occurs, at about 8 p.h.r. added thermoplastic, this becomes less rapid and a slower decrease in E is then observed as the amount of added thermoplastic is further increased. It is noteworthy that there are no discontinuities apparent in the data as the microstructure of the multiphase polymer changes from being thermoplastic-particulate, to co-continuous, to phase-inverted as the amount of thermoplastic increases.

3.1.3. Fracture properties

The dependence of the stress-intensity factor, K_{Ic} , at the onset of crack growth and the fracture energy, G_{Ic} , as a function of the concentration of added thermoplastic are shown in Figs 5 and 6, respectively. In Fig. 5 there is an initial decrease in the value of K_{Ic} , and this is a reproducible and significant decrease. This suggests that the single-phase microstructure of thermoplastic dissolved in the epoxy polymer does not

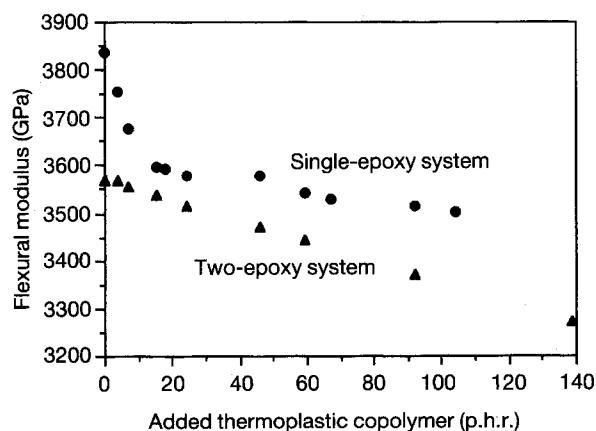


Figure 4 Flexural modulus of thermoplastic-toughened epoxy materials as a function of added thermoplastic poly(ether sulphone) copolymer concentration.

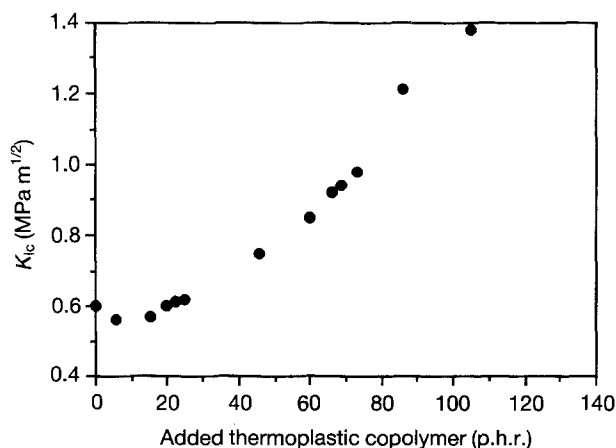


Figure 5 Stress-intensity factor, K_{Ic} , at the onset of crack growth as a function of added thermoplastic poly(ether sulphone) copolymer concentration. (Single-component epoxy-resin system.)

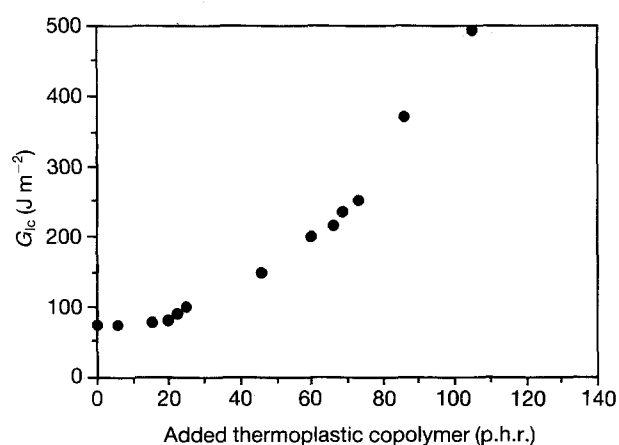


Figure 6 Fracture energy, G_{Ic} , as a function of added thermoplastic poly(ether sulphone) copolymer concentration. (Single-component epoxy-resin system.)

give any toughening effect. However, from about 10 p.h.r. added thermoplastic there is a steady increase in the value of K_{Ic} , consistent with the onset of phase separation. However, it should be noted that there are no obvious discontinuities in the plot of K_{Ic} versus concentration of added thermoplastic and, in particular, there are no abrupt changes in the toughness when the microstructure changes from particulate thermoplastic to co-continuous (at about 50 p.h.r.) and then to phase-inverted (at about 80 p.h.r.).

The variation of G_{Ic} with concentration of thermoplastic is shown in Fig. 6. The initial decline in the toughness is now not observed. This simply arises from the fact that both E and K_{Ic} decrease rapidly as the thermoplastic concentration is increased from 0 to about 10 p.h.r., and when G_{Ic} is evaluated from Equation 3 the value for G_{Ic} is found to be approximately constant. As the amount of thermoplastic is increased from about 10 to about 100 p.h.r. the value of G_{Ic} steadily increases, but again there are no obvious discontinuities when the microstructure changes from one type to another type. The value of G_{Ic} for the pure epoxy polymer is about 75 J m^{-2} and this rises to a

maximum of about 500 J m^{-2} at the maximum thermoplastic concentration of about 100 p.h.r.

3.1.4. Fractographic studies

A series of scanning electron micrographs of the various fracture surfaces is shown in Fig. 7. The surfaces of the pure epoxy (Fig. 7a) and the materials containing a thermoplastic-particulate phase (Fig. 7b) are both relatively featureless, apart from the clear presence of the particles in the latter. The fracture surfaces of the co-continuous and phase-inverted materials were indistinguishable, and the former is shown at both a low and a high magnification in Figs 7c and d. From Fig. 7c it is evident that crack growth has occurred through both phases and is essentially brittle in nature. The higher magnification micrograph shown in Fig. 7d clearly confirms that the two phases contain sub-inclusions which appear as small nodules on the fracture surface.

It had been hoped that the scanning electron micrographs would indicate the toughening mechanisms which are responsible for the significant increase in toughness, when the reactively terminated poly(ether sulphone) copolymer is added to the epoxy and phase separation occurs. However, no definitive evidence of any recognized toughening mechanism was found in the micrographs. For example, there are no signs (i) of cavitation or debonding of the particulate phase, or (ii) of plastic yielding of the epoxy-rich or thermoplastic-rich phases. From Fig. 7c the crack must clearly be deflected as it advances, and it is established that this will lead to an increase in G_{Ic} . On the other hand the extent of crack deflection for the thermoplastic-particulate material is minimal. Also, of course, in the materials with the co-continuous and phase-inverted microstructures, the crack must advance through fracture of the thermoplastic-rich phase, and this phase will undoubtedly be tougher than the epoxy-rich phase.

3.1.5. Structure-property relationships

From the above detailed studies it was hoped that definitive relationships between the microstructure and fracture properties could be established, and that the toughening mechanisms could be clearly identified. However, as discussed in detail below, the complex nature of the materials precludes such straightforward interpretations.

Now the toughness of the materials does not begin to increase until phase separation of the thermoplastic copolymer occurs (at about 8 p.h.r. added thermoplastic copolymer). Until this point, a single-phase solution of the thermoplastic copolymer in the epoxy is formed and the value of K_{Ic} , which reflects the load-carrying capacity of the material, actually falls somewhat as the concentration of the thermoplastic copolymer is initially increased; and the value of G_{Ic} , which reflects the capability of the materials to withstand an applied strain or strain-energy, is virtually constant. As the concentration of poly(ether sulphone) copolymer is further increased, the values of K_{Ic} and G_{Ic}

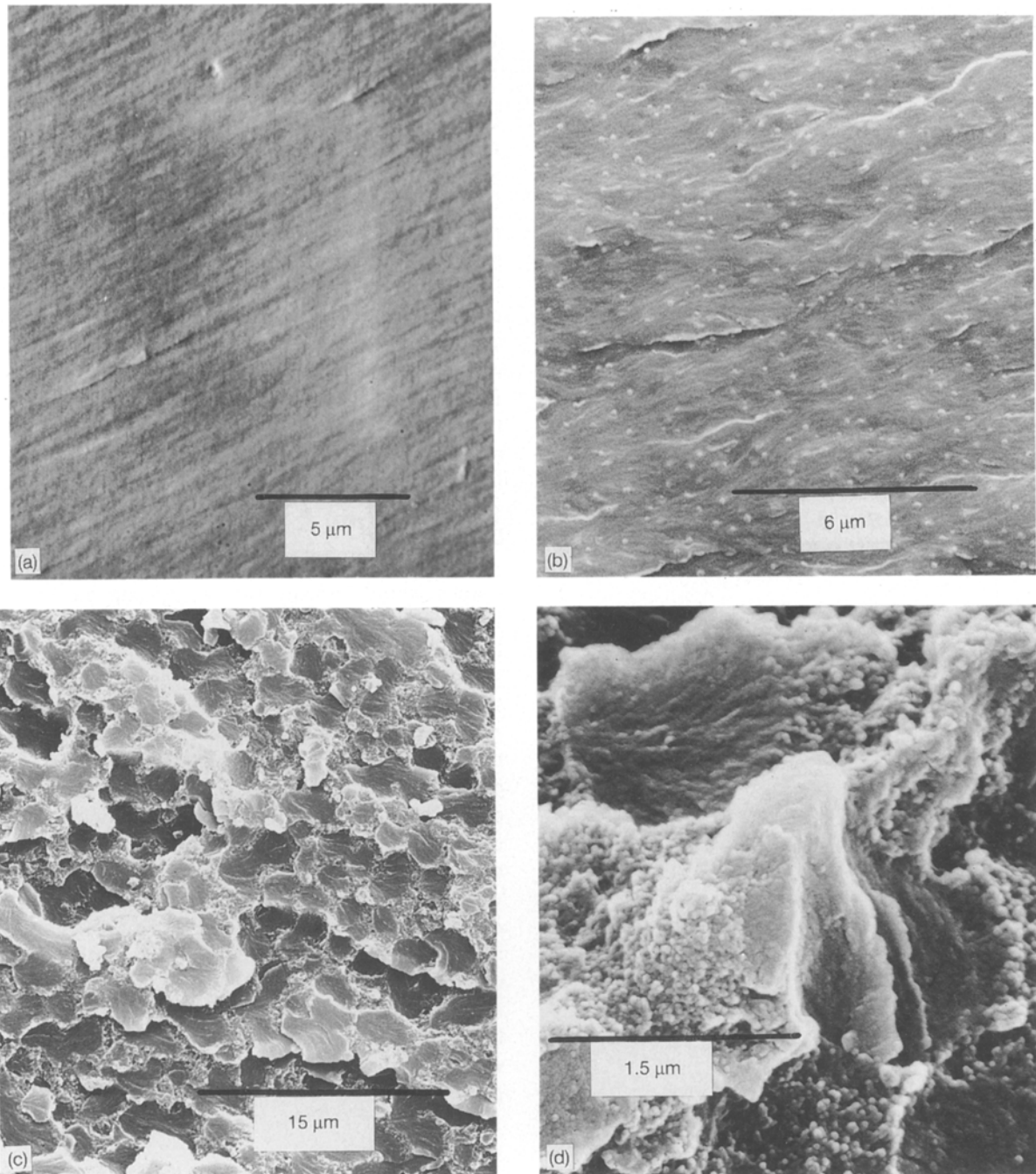


Figure 7 Scanning electron micrographs of the fracture surfaces from the following microstructures of the single-component epoxy-resin system: (a) single phase – epoxy-rich continuous phase; (b) particulate – second phase of thermoplastic-rich particles in continuous epoxy-rich matrix; (c) co-continuous or phase-inverted; (d) co-continuous or phase-inverted – higher magnification than (c).

increase steadily. There are no obvious discontinuities as the microstructure changes from particulate to co-continuous to phase-inverted, although the rate of increase in K_{Ic} and G_{Ic} is greater when the level of added thermoplastic copolymer exceeds about 55 p.h.r., and this is approximately the concentration at which the co-continuous thermoplastic phase is first observed. Therefore, it appears that phase separation is required in order to achieve a significant increase in the toughness of the thermoplastic-modified epoxy polymers. Further, there is some evidence that the attainment of either a co-continuous or a phase-inverted microstructure imparts a higher toughness to the multiphase material than expected from that of the measured toughness of a thermoplastic-particulate

microstructure. However, there is no evidence that a phase-inverted microstructure inherently results in a higher toughness compared to that obtained in a co-continuous material, because the higher toughness seen in the former material may simply be a result of the greater concentration of added thermoplastic copolymer present. Unfortunately, it is not possible to resolve this point. Because it is impossible to prepare a co-continuous microstructure with added concentrations of thermoplastic copolymer of more than 83 p.h.r., as phase-inversion occurs at this level of added copolymer.

Early work by Bucknall and Partridge [8] used a non-reactive poly(ether sulphone) and no increase in toughness was found, whether phase separation

resulted or not. More recently, MacKinnon *et al.* [17] have used a reactively terminated poly(ether sulphone) to modify epoxy resins, and reported that phase separation was needed in order to record a significant increase in the toughness, but no discontinuities in the plots of K_{Ic} or G_{Ic} versus the concentration of added thermoplastic were observed as the microstructure changed from one form to another. Also, Wilkinson *et al.* [20] have used a reactively terminated polysulphone to modify thermosetting bis-maleimide resins and reported increases in toughness of the order found in previous studies on thermoplastic modifiers and in the present study. However, they found no correlation between the toughness and the various microstructures which were observed. Considering other thermoplastic modifiers, Bucknall and Gilbert [13] found that phase separation was needed in order to record a significant increase in the toughness of epoxy polymers modified with a poly(ether imide), but again did not observe any discontinuities in the plots of K_{Ic} or G_{Ic} versus the concentration of added thermoplastic as the microstructure changed from one form to another. Similar conclusions were reached by Hourston and Lane [16], who also employed a poly(ether imide) modifier. The above observations are obviously all in broad agreement with the present work. On the other hand, Murakami *et al.* [18] have reported that, in their studies on an epoxy modified with a poly(ether imide), the simple attainment of a multiphase polymer possessing particles of thermoplastic-rich polymer was insufficient to result in an increase in toughness. They found that it was necessary to achieve a phase-inverted microstructure, where the poly(ether imide) was the continuous phase, to observe an increase in toughness.

Another aspect to consider is the importance of the thermoplastic copolymer dissolving in the epoxy-rich phase. This will reduce the effective cross-link density of the epoxy phase, and this may lead to an increase in the toughness of the epoxy-rich phase. However, when up to 8 p.h.r. thermoplastic copolymer is added, the thermoplastic all dissolves in the epoxy and, as stated above, this appears to give no significant increase in toughness; and indeed a decrease in K_{Ic} is observed. At higher levels of added thermoplastic, and when a multiphase microstructure is always now present, the concentration of thermoplastic in the epoxy-rich phase steadily increases from 0 to 17.5%. Nevertheless, because a concentration of 8 p.h.r. thermoplastic in the epoxy phase (i.e. the single-phase material with 8 p.h.r. added thermoplastic) does not show any significant improvement in toughness, it seems unlikely that even a level of 17.5% thermoplastic dissolved in the epoxy-rich phase will result in any major increase in toughness. Thus, it seems unlikely that the thermoplastic copolymer dissolving in the epoxy-rich phase is responsible for any significant increase in the toughness of the multiphase material, although in theory such an effect might be expected to increase the toughness of the epoxy-rich phase via effectively reducing the cross-link density of the epoxy-rich phase.

Another, similar consideration is the concentration of epoxy in the thermoplastic-rich phase. In this case

there is epoxy dissolved in the thermoplastic-rich phase, when this phase is in a particulate, co-continuous or phase-inverted form. The concentration of such dissolved epoxy rises from 0 to about 40% as the amount of added thermoplastic copolymer is increased from 8 p.h.r. to 100 p.h.r. Further, for the co-continuous and phase-inverted microstructures there are also small sub-inclusion particles of epoxy present in the thermoplastic-rich phases. Now an intriguing question is whether epoxy present in the thermoplastic-rich phase would greatly increase the toughness of this phase, bearing in mind that the epoxy is present in the thermoplastic-rich phase both (i) dissolved in the thermoplastic-rich phase, and/or (ii) as small sub-inclusions of phase-separated epoxy particles. With a typical engineering thermoplastic of high molecular weight, the presence of epoxy in the thermoplastic-rich phase would be expected to make little or no contribution to the toughness of the thermoplastic. However, the present thermoplastic copolymer has a relatively low molecular weight $M_n \approx 10\,000$ and is, therefore, a relatively very brittle material. Now the molecular weight of the thermoplastic poly(ether sulphone) copolymer could be increased by chain extension through its reactive end-groups with the epoxy, and such chain extension reactions are known to be possible and to lead to an increase in toughness of the thermoplastic [21]. Further, with such a thermoplastic copolymer, the presence of phase-separated particles of epoxy material would be beneficial to the basic toughness. Therefore, it seems likely that the presence of epoxy in the thermoplastic-rich phase could increase the toughness of this phase.

Considering the size of the main phase-separated domains, the particles of the thermoplastic-rich phase are about 0.2–0.4 μm diameter and the co-continuous ribbons of thermoplastic-rich phase are about 0.5–2 μm wide. The continuous matrix of the thermoplastic-rich material between the epoxy-rich particles in the phase-inverted microstructure is also of a similar dimension; namely 0.5–1 μm wide. Therefore, there appears to be no direct correlation of toughness with the size of the phase-separated domains.

Turning to the basic mechanisms responsible for the increase in measured toughness, Kim and Brown [11] have suggested that plastic yielding of the epoxy-rich and thermoplastic-rich phases were the active toughening mechanisms in the thermoplastic-modified epoxy polymers which they investigated. Bucknall and Gilbert [13] and Hedrick *et al.* [15] have concluded that ductile tearing in the thermoplastic-rich phase is a major mechanism, but did not observe any plastic yielding of the epoxy-rich phase. According to this view, the first stage of fracture is brittle failure of the epoxy-rich phase, leaving the more ductile thermoplastic-rich phase bridging behind the advancing crack front. Both these groups of workers supported their suggestions by observing plastic drawing and ductile failure of the thermoplastic-rich phase on the fracture surfaces of the materials. However, the evidence in the literature for plastic deformation and ductile failure of the thermoplastic particles is limited. For example, in the above-mentioned studies, such

failures were not always observed, even when an appreciable increase in toughness was recorded for the multiphase thermoplastic-modified epoxy polymer. Also, other authors [12, 16] have not observed any significant ductile tearing of the thermoplastic-rich phase in their studies. In the present work there are no clearly identifiable toughening mechanisms. For example, as noted previously, there are no indications (i) of cavitation or debonding of the particulate phase (as has been observed in rubber-toughened epoxy polymers [2-7]), or (ii) of plastic yielding of the epoxy-rich or thermoplastic-rich phases. From Fig. 7c the crack must clearly be deflected as it advances in the co-continuous or phase-inverted material, and it is established [22, 23] that this will lead to an increase in G_{Ic} . On the other hand, the extent of crack deflection for the thermoplastic-particulate material is minimal. Another factor to consider, is that in the materials with the co-continuous and phase-inverted microstructures, the crack must advance by fracture of the thermoplastic-rich phase, and from the above discussions it is considered that this phase, when chain-extended by the epoxy to increase the molecular weight of the poly(ether sulphone) copolymer, will undoubtedly be tougher than the epoxy-rich phase. Thus, as a result of the microstructure, the crack is now forced to advance through the thermoplastic-rich phase, and this must lead to an increase in the measured toughness.

3.2. The two-component epoxy-resin system

The above studies were also conducted using a two-component epoxy-resin system. This consisted of the triglycidyl aminophenol epoxy and a difunctional epoxy, namely the diglycidyl ether of bisphenol F. The ratio of the two resins was 1:1.05 and the curing agent was again 4,4'-diaminodiphenylsulphone. Materials were prepared and cured using various concentrations of the reactively terminated poly(ether sulphone) copolymer, as before.

Scanning electron microscopy was used to identify the microstructures. Again up to concentrations of about 8 p.h.r. added thermoplastic, no phase separation occurred, then at higher concentrations thermoplastic-rich particles phase-separated. These particles were considerably smaller than those observed when the triglycidyl aminophenol epoxy was used alone, being about 0.05 μm in size for the two-epoxy system compared to 0.3 μm for the triglycidyl aminophenol epoxy. At concentrations above about 45 p.h.r., a co-continuous microstructure was observed, and again the width of the ribbons of the thermoplastic-rich phase were considerably smaller for the two-epoxy system; being about 0.05 μm in size compared to 1.5 μm . In contrast to the single-epoxy system, there was no transition of the co-continuous to a phase-inverted microstructure with the two-epoxy system.

The dynamic mechanical analysis of the two-component system revealed that the two epoxies were compatible and formed a single phase, the T_g of the cured diglycidyl ether of bisphenol F being about 96 °C whilst the T_g of the cured two-epoxy system was

about 200 °C. Thus, the two-epoxy system containing the added thermoplastic always tended to exhibit one broad $\tan \delta$ peak between about 170 and 230 °C with a maximum at about 200 °C.

The flexural modulus is shown as a function of the concentration of added thermoplastic in Fig. 4. There is a steady decrease in the value of E as the thermoplastic is added and, as expected, the modulus of the two-epoxy system, which contains a difunctional epoxy, is always somewhat lower than that of the trifunctional epoxy when used alone.

The variations of K_{Ic} and G_{Ic} with concentration of thermoplastic are shown in Figs 8 and 9, respectively. For both K_{Ic} and G_{Ic} the toughness initially decreases, and then increases steadily as the concentration of added thermoplastic copolymer is increased. These observations are in general agreement with the previous results for the single-epoxy system, where it was found that the formation of a multiphase material was required for any significant increase in toughness to occur. However, at higher concentrations of about 50 p.h.r. the toughness of the two-component system is markedly inferior to that of the single-epoxy system. In the case of G_{Ic} the results are shown in Figs 6 and 9,

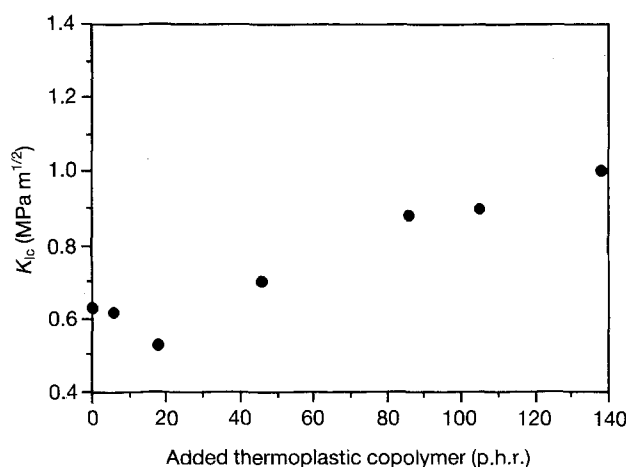


Figure 8 Stress-intensity factor, K_{Ic} , at the onset of crack growth as a function of added thermoplastic poly(ether sulphone) copolymer concentration. (Two-component epoxy-resin system.)

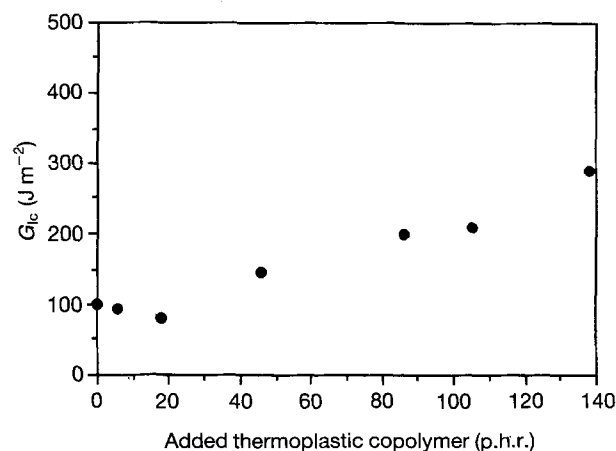


Figure 9 Fracture energy, G_{Ic} , as a function of added thermoplastic poly(ether sulphone) copolymer concentration. (Two-component epoxy-resin system.)

and below about 50 p.h.r. added thermoplastic, the increase in G_{Ic} is very similar for the two-epoxy system as for the single-epoxy system. However, again at higher concentrations, the thermoplastic has a far greater effect on the toughness when added to the single-epoxy system.

Interestingly, both the two-epoxy and single-epoxy system possess co-continuous microstructures over the range of thermoplastic copolymer levels between about 50 and 83 p.h.r.; but at higher levels the single-epoxy system exhibits phase inversion whilst the two-epoxy system appears to continue to exhibit a co-continuous microstructure. Nevertheless, even over this range the single-epoxy system shows an increased toughness compared to the two-epoxy system. The increased toughness of the former material is, therefore, observed well before the single-epoxy system material exhibits a phase-inverted microstructure. Thus, again, there is no evidence that a phase-inverted microstructure inherently results in a higher toughness compared to that obtained in a co-continuous material.

4. Conclusions

The microstructure of a triglycidylaminophenol epoxy cured with 4,4' diaminodiphenylsulphone and containing various concentrations of a reactively terminated poly(ether sulphone) copolymer has been characterized in detail, and shown to vary as the amount of the thermoplastic copolymer is steadily increased. At low concentrations of the added poly(ether sulphone) copolymer a single-phase microstructure is obtained, which changes to a particulate microstructure of thermoplastic-rich particles in an epoxy-rich matrix, then to a co-continuous structure and then to a phase-inverted form. Further, the thermoplastic-rich and epoxy-rich phases are complex in nature, with each phase containing, either in solution or as sub-particles, epoxy or thermoplastic respectively. Considering the effect of the microstructure on the toughness, there is an initial decrease in the value of K_{Ic} as the concentration of added copolymer is increased, which suggests that the single-phase microstructure of thermoplastic dissolved in the epoxy polymer does not give any toughening effect; thereafter, the value of K_{Ic} increases steadily with concentration of added thermoplastic. The value of G_{Ic} is constant until phase separation occurs, and then increase steadily with concentration of poly(ether sulphone) copolymer. However, whether the values of K_{Ic} or G_{Ic} are considered, there are no obvious discontinuities in the plots of K_{Ic} or G_{Ic} versus concentration of added thermoplastic and, in particular, there are no abrupt changes in the toughness when the microstructure changes from particulate thermoplastic to co-continuous and then to phase-inverted.

Similar studies were also conducted using a two-component epoxy-resin system. This consisted of the triglycidyl aminophenol epoxy and a difunctional epoxy, namely the diglycidyl ether of bisphenol F. The ratio of the two resins was 1 : 1.05 and the curing agent was again 4,4' diaminodiphenylsulphone. Materials were prepared and cured using various concentrations

of the reactively terminated poly(ether sulphone) copolymer, as before. In contrast to the single-epoxy system, the microstructure changed from single-phase, to particulate to co-continuous, as the amount of the thermoplastic copolymer is steadily increased; no phase inversion being observed with the two-component epoxy-resin system. For both K_{Ic} and G_{Ic} the toughness initially decreases, and then increases steadily as the concentration of added thermoplastic copolymer is increased. These observations are in general agreement with the previous results for the single-epoxy system, where it was found that the formation of a multiphase material was required for any significant increase in toughness to occur. However, at higher concentrations of about 50 p.h.r. the toughness of the two-component system is markedly inferior to that of the single-epoxy system.

Considering the structure-property relationships, it appears that phase separation is required in order to achieve a significant increase in the toughness of the thermoplastic-modified epoxy polymers. Further, there is some evidence that the attainment of either a co-continuous or a phase-inverted microstructure imparts a higher toughness to the multiphase material than expected from that of the measured toughness of a thermoplastic-particulate microstructure. However, there is no evidence that a phase-inverted microstructure inherently results in a higher toughness compared to that obtained in a co-continuous material, because the higher toughness seen in the former material may simply be a result of the greater concentration of added thermoplastic copolymer present.

The micromechanisms of fracture have been studied and there are no indications (i) of cavitation or debonding of the particulate phase, or (ii) of plastic yielding of the epoxy-rich or thermoplastic-rich phases. However, the crack must clearly be deflected as it advances in the co-continuous or phase-inverted material, and this will lead to an increase in toughness. Also, in the materials with the co-continuous and phase-inverted microstructures the crack must advance by fracture of the thermoplastic-rich phase, and it is considered that this phase, when chain-extended by the epoxy to increase the molecular weight of the poly(ether sulphone) copolymer, will undoubtedly be tougher than the epoxy-rich phase. Thus, when the microstructure forces the crack to advance through the thermoplastic-rich phase, this leads to an increase in the measured toughness.

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