The Morphology and Fracture Properties of Thermoplastic-Toughened Epoxy Polymers

R. D. Brooker[a]; A. J. Kinloch[a]; A. C. Taylor[a]

[a] Department of Mechanical Engineering, Imperial College London, South Kensington Campus, London, UK

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Department of Mechanical Engineering, Imperial College London, South Kensington Campus, London, UK

The present work investigates the effect on the morphology, fracture performances, and tensile properties of an epoxy polymer when modified with various percentages of a thermoplastic-polymeric toughener. The thermoplastic toughener was a poly(ether sulfone) copolymer with reactive end-groups. It was initially soluble in the epoxy-resin/hardener mixture but phase separated during the curing of the epoxy resin. After the epoxy had cured, the thermoplastic toughener, when present at relatively low concentrations, possessed a spherical-particulate morphology in an epoxy-rich continuous phase. However, as the weight percentage of the thermoplastic was increased the morphology changed to a co-continuous microstructure, and then to a phase-inverted microstructure of epoxy spherical particles in a thermoplastic-rich continuous phase. The Young's modulus and 0.2% proof stress of the epoxy polymer were relatively unaffected by the addition of the thermoplastic, whilst the ultimate tensile strength increased with increasing thermoplastic content. The fracture toughness and fracture energy of the formulations were found to increase steadily with increasing thermoplastic content. This increase was not, however, linked to the observed changes in morphology, but simply to the weight-percentage of the thermoplastic toughener added to the formulation.

1. INTRODUCTION

Epoxy polymers typically have a good thermal stability and a high Young's modulus, which are desirable properties for their use as adhesives and as matrices in fibre-composite materials. However, epoxy polymers tend to be brittle and much work has been focused on how to increase their fracture toughness and fracture energy whilst not compromising their modulus and thermal stability, *e.g.*, [1,2]. For example, rubbery polymers have been used in various studies [3,4] to increase the fracture energy of thermoset polymers. However, rubbery tougheners have been shown to typically decrease the thermal stability and Young's modulus, which can be unacceptable for some fibre-composite applications. An alternative route is to use a thermoplastic-polymeric toughener and such tougheners have been found to increase the fracture properties of epoxy polymers, whilst imparting better thermal stability and resulting in less of a reduction in Young's modulus than when using rubbery tougheners [2,5,6].

The present paper describes the use of a poly(ether sulfone) copolymer to toughen an epoxy polymer. Tensile and fracture tests were carried out and the material was analysed to identify its morphology. Of particular interest was to explore the observation that whilst some previous authors have suggested that the changes in morphology of the blend significantly affect the fracture properties [5,7], other authors have argued that it is simply the increase in thermoplastic content, not the change in morphology, which leads to improved fracture properties [2].

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The epoxy resin used was a mix of a diglycidyl ether of bisphenol F (DGEBF), (PY306), and a triglycidyl aminophenol (TGAP), (MY0510). Both were manufactured by Huntsman (Basel, Switzerland). The curing agent was an amine hardener, 4,4'-methylenebis-(3-chloro 2,6-diethylaniline) (MCDEA), from Lonza (Basel, Switzerland). They were used in a constant ratio by weight of 1 part PY306:1.17 parts MY0510:1.42 parts MCDEA [8]. The thermoplastic toughener was a poly(ether sulfone) copolymer which was supplied in powder form by Cytec Engineered Materials, Wilton, UK. It possessed reactive end-groups.

The tensile and fracture specimens were machined from 5-mm thick plates of polymer, and these plates were cast as described below.

For the sample with no thermoplastic, the two epoxies were poured into a Pyrex® beaker, then stirred using a spatula before the MCDEA was added. The mix was placed in an oven at 120°C and stirred for 1 h at about 200 rpm using an overhead stirrer fitted with a radial-flow impeller. This ensured that the MCDEA dissolved fully into the epoxy.

For plates that included the thermoplastic toughener, after the two epoxies had been combined, the thermoplastic powder was added. The mix was stirred using the overhead stirrer at 650 rpm and 120°C for at least 2 h until all of the thermoplastic had dissolved. The MCDEA was then added and stirred for 1 h at 650 rpm and 120°C. When 25 wt.%, or greater, of the thermoplastic was required, the thermoplastic was added in two batches of approximately equal weight, each batch being stirred for 2 h at 650 rpm and 120°C. The mix was allowed to cool overnight and was re-heated the following day, when the MCDEA was added as described above.

The plates were formed using a picture-frame mould. This was cleaned, coated with a layer of Frekote 700-NC, from Loctite (Hatfield, UK), and sealed with a silicone sealant. The mould and its lid were pre-heated to 80°C. If the resin mixture had a relatively low viscosity then, once the resin and MCDEA were fully mixed, the mould was partially filled with the resin. The mould and the remaining resin in the beaker were placed in a vacuum oven to be degassed at 80°C. Once this degassing had been completed, the lid was placed on the mould, leaving gaps at both sides, and clamped in place. Extra resin was then poured into the mould from one side, so that the mould filled up to the top and the air could escape from the other side, without entrapping air bubbles. When the thermoplastic additive was used, the viscosity was sufficiently high that the resin was first degassed in a vacuum oven at 100°C in the beaker. The resin was then transferred to the mould, which was slightly overfilled, and degassed again. The lid was lowered in place and clamped with G-clamps. A thermocouple was placed in the mould to monitor the temperature of the mixture to check that the plates were all cured at the same temperature and for the same length of time. The epoxy/thermoplastic blends were cured in an oven, heating the blend at 1°C/min and then holding at 180°C for 5 h. The plates were allowed to cool to room temperature in the mould and were then removed.

2.2. Morphological and Thermal Studies

To examine the morphology, an ultramicrotome from RMC Products (Tucson, AZ, USA) was used to prepare flat surfaces at room temperature ready for examination using a Veeco atomic force

microscope (AFM). The AFM produced both a height and a phase image; the height image clearly shows any areas which are raised above other areas, and the phase image shows the "hardness" of the surface so that different materials of different hardness values are easily distinguished. Dynamic mechanical thermal analysis (DMTA) was carried out using a Tritec 2000 DMA from Triton Technology (Keyworth, UK), set-up in a dual cantilever bending mode, to measure the effect on the glass transition temperature, T_g, of the cured epoxy polymer with and without the addition of the thermoplastic. A scanning electron microscope, a S3400 from Hitachi High-Technologies (Maidenhead, UK) was used to examine the fracture surfaces, which were first sputter-coated with gold.

2.3. Mechanical Properties

Tensile specimens were cut from the plates made as described above according to BS EN ISO 527-2 [9], using test geometry 5A. Compact-tension samples were cut to BS ISO 13586 [10], with overall dimensions of $40 \times 38.4 \times 5$ mm. The notch was machined, and then a natural pre-crack was formed by tapping a razor blade into the notch.

The tensile tests were carried out at 1 mm/min and room temperature, using a clip-gauge extensometer to measure accurately the displacement of the gauge-length. The Young's modulus, ultimate tensile strength (UTS), and 0.2% proof stress were calculated. The fracture tests were carried out at a loading rate of 1 mm/min and at room temperature. The fracture toughness, K_{IC}, and fracture energy, G_{IC}, were calculated from the measured data. The energy method was used for calculating values of G_{IC} [10].

3. RESULTS

3.1. Microstructure

The microtomed samples of each of the epoxy/thermoplastic blend formulations were examined using the AFM. The phase images from micrographs showed the morphology less well than the height images. This is a result of the thermoplastic having a similar hardness to that of the epoxy. However, they have somewhat different cutting resistances when microtomed. This leads to the thermoplastic phase being revealed as a raised region, which is approximately 10 nm higher than the epoxy phase. The AFM height-images are shown in Fig. 1. The unmodified epoxy is smooth and featureless, as would be expected for a homogeneous thermoset polymer (Fig. 1a). When 15 or 20 wt.%
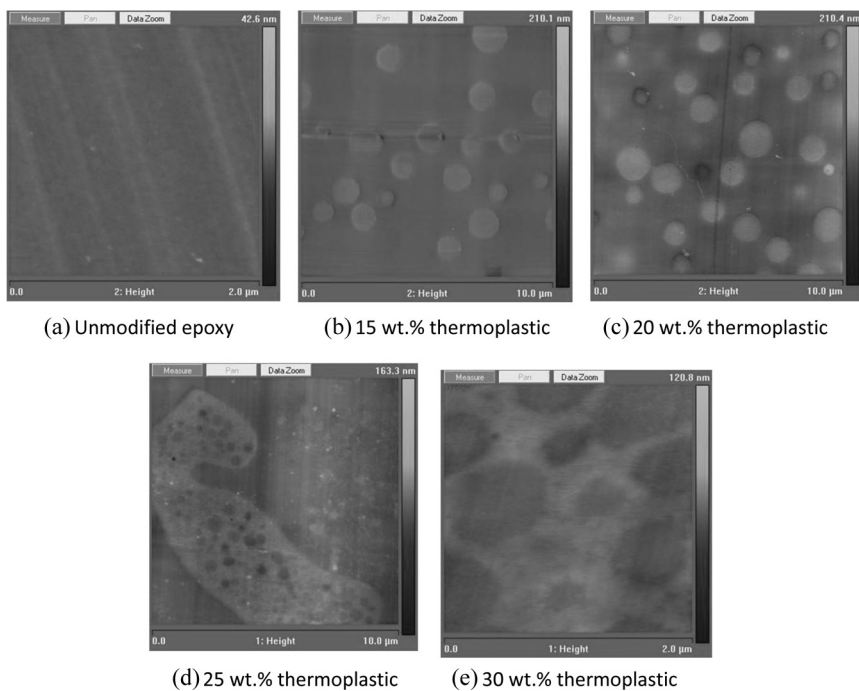
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(a) Unmodified epoxy (b) 15 wt.% thermoplastic (c) 20 wt.% thermoplastic

(d) 25 wt.% thermoplastic (e) 30 wt.% thermoplastic

FIGURE 1 AFM images of samples of epoxy with (a) 0, (b) 15, (c) 20, (d) 25, and (e) 35 wt.% thermoplastic toughener showing the change from a spherical particulate morphology of thermoplastic particles in an epoxy-rich continuous phase at 15 and 20 wt.% thermoplastic, to a co-continuous morphology for the epoxy- and thermoplastic-rich phases at 25 wt.%; and a phase inverted morphology of epoxy particles in a thermoplastic-rich continuous phase at 35 wt.%.

of the poly(ether sulfone) copolymer is added, the thermoplastic phase-separates into spherical particles, which have a diameter of approximately 1 μm, and which are well dispersed in the epoxy-rich continuous-phase, as shown in Figs. 1b and 1c. The particles also appear to be well-bonded to the epoxy, as there is no evidence of debonding from the epoxy during microtoming. (It is noteworthy that debonding of the thermoplastic particles was observed during micro-toming for the same thermoplastic but which possessed unreactive end-groups [11]). However, when the percentage of thermoplastic was increased to 25 wt.%, the morphology becomes co-continuous (Fig. 1d), with interpenetrating regions of the thermoplastic-rich phase and the epoxy-rich phase. There is also some localised phase-inversion within the thermoplastic-rich phase, which may be

observed as small spheres of epoxy polymer in the thermoplastic phase. The epoxy spheres within the thermoplastic are up to 0.6 μm in diameter and there are also thermoplastic spheres in the epoxy-rich phase with a diameter of 0.5 μm.

Finally, the percentage of thermoplastic was increased to 35 wt.% and the morphology was found to become a phase-inverted type, *i.e.*, with the epoxy polymer now forming well-dispersed phase-separated particles, approximately 1 μm in diameter, within a thermoplastic-rich continuous-phase (Fig. 1e). No higher weight percentages of thermoplastic toughener in the formulations could be achieved, as the mixture became too viscous for casting the sheets.

To establish whether the thermoplastic was fully phase-separating on curing of the epoxy polymer, the percentage of thermoplastic which was added was firstly converted to a volume percentage. Secondly, the AFM images were analysed using the "blob analysis" routine in the Global Lab image 2 software from Data Translation Inc., (Marlborough, MA, USA). This software calculates the area percentage of the image which belongs to each phase according to its colour, and the area fraction of the phase is equal to the volume fraction of that phase [12]. The percentages of the thermoplastic, calculated both from the weight percentages added and from the image-analysis studies, are given in Table 1. These data show that when the morphology consists of spherical particles of the thermoplastic toughener, *i.e.*, at 15 and 20 wt.% additions of the poly(ether sulfone) copolymer, the thermoplastic and epoxy both almost fully phase-separate. At 25 and 35 wt.% of the added thermoplastic, the percentage of the phase which is thermoplastic-rich appears to be significantly higher than would be expected if the thermoplastic and epoxy had fully phase-separated. This implies that some of the epoxy is now present in a significant concentration in the thermoplastic-rich phase.

Dynamic mechanical thermal analysis (DMTA) was performed using the various formulations. However, as expected, the glass

TABLE 1 Percentages of Thermoplastic Calculated from the Percentage of Material Included and from the Amount Apparent in the AFM Images

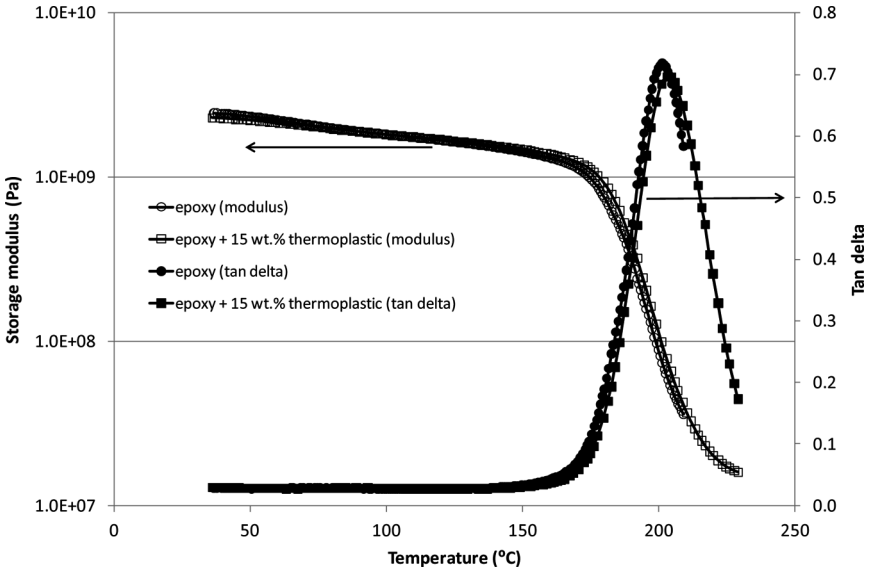| Added thermoplastic content (wt.%)	Added thermoplastic content (vol.%)	Thermoplastic content from image analysis (vol.%)
15	13.5	14.5
20	18.1	19.2
25	22.8	33.1
35	32.3	46.2

FIGURE 2 DMTA results for the epoxy polymer and the epoxy/15 wt.% thermoplastic-toughener polymer.

transition temperatures, T_g, of the epoxy and the thermoplastic materials are almost identical; the T_g of the thermoplastic was said to be of the order of 200°C [8]. As such, the DMTA results for the epoxy polymers, with and without added thermoplastic, are virtually identical. This can be seen in Fig. 2. Thus, no conclusions about the separation of the phases can be determined from this test method. With measurements taken at 10 Hz, the T_g for the epoxy was found to be $201 \pm 1°C$ and for the epoxy with 15 wt.% thermoplastic it was $203 \pm 1°C$.

3.2. Tensile Properties

Tensile tests were carried out to determine the Young's modulus, ultimate tensile strength, UTS, and yield strength of the epoxy and epoxy/thermoplastic blends. The results for the UTS and Young's modulus are shown in Fig. 3, where the observed microstructure is also summarised. Table 2 gives the full results as a function of added thermoplastic, including values of the standard deviation (SD).

The results for the 0.2% proof stress show no significant change with the addition of thermoplastic toughener (Table 2). However,
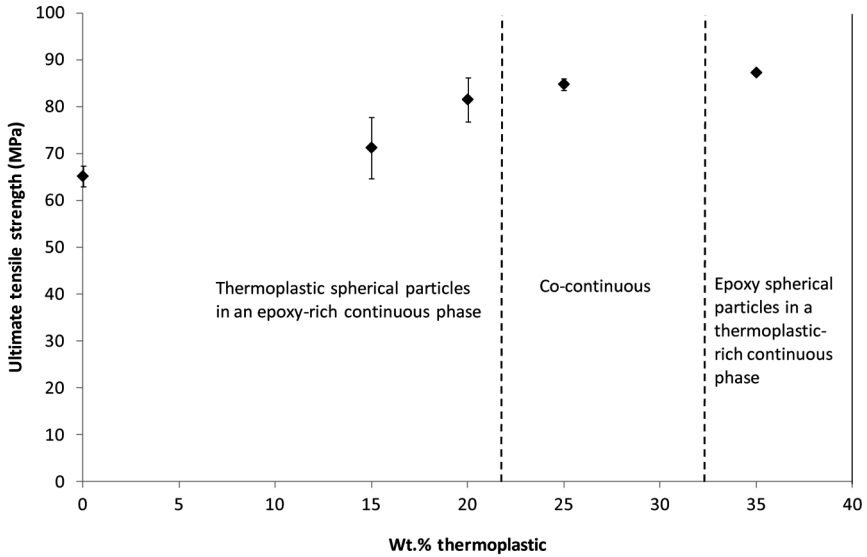
(a) Ultimate tensile strength
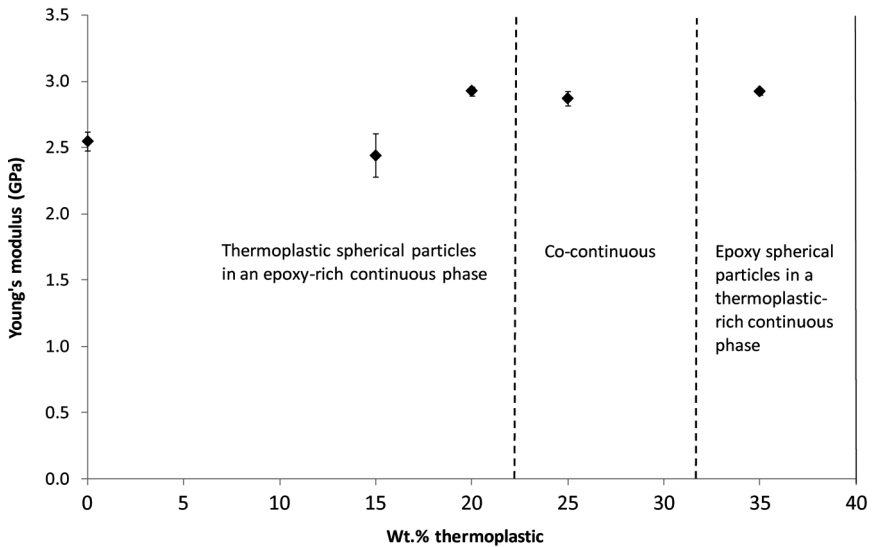
(b) Young's modulus

FIGURE 3 Values of the ultimate tensile strength, UTS, and Young's modulus for the epoxy polymer with increasing amounts of thermoplastic toughener.

TABLE 2 Tensile Results for Thermoplastic-Modified Epoxy Polymer

Thermoplastic content (wt.%)	Young's modulus (GPa)		Ultimate tensile strength (MPa)		0.2% Proof stress (MPa)	
	Mean	SD	Mean	SD	Mean	SD
0	2.55	0.07	65.2	2.3	44.8	1.5
15	2.44	0.16	71.2	6.6	43.0	3.2
20	2.93	0.03	81.5	4.6	45.8	0.4
25	2.87	0.05	84.8	1.3	44.9	3.3
35	2.92	0.03	87.2	0.4	45.3	1.1

there is a steady increase in the value of the UTS as the content of the poly(ether sulfone) thermoplastic copolymer is increased, as shown in Fig. 3a. This confirms there is good adhesion between the epoxy and the thermoplastic phases, as poor bonding would result in a decrease in the UTS [13].

For the values of the Young's modulus, definitive trends are harder to draw. The modulus values for the epoxy polymer containing 0 and 15 wt.% of the thermoplastic toughener are the same, within experimental error. However, when 20 wt.% thermoplastic is added, the modulus is somewhat higher. The moduli for the epoxy polymers containing 25 and 35 wt.% thermoplastic toughener are similar to that for the polymer containing 20 wt.% of the thermoplastic (Fig. 3b). Thus, there is no progressive increase in modulus with increasing thermoplastic content, and the relatively small step change that occurs between 15 and 20 wt.% of added thermoplastic is not associated with any distinct change of morphology, as may be seen from Fig. 3b.

The strain to failure increases significantly as the percentage of thermoplastic toughener in the epoxy polymer increases. This can be seen in Figure 4, where the stress *versus* strain curves for the unmodified epoxy polymer, and samples containing 20 and 35 wt.% of thermoplastic toughener, are given. The epoxy and thermoplastic modified epoxy have similar T_g values and moduli, but the thermoplastic modified epoxy shows a higher ductility. When comparing the stress *versus* strain curves for the 20 and 35 wt.% of added thermoplastic it can be seen that the traces are almost identical, except that the epoxy polymer containing 20 wt.% of thermoplastic toughener fails before the 35 wt.% sample. Both of these samples have a particulate morphology, with spherical particles of about 1 μm in diameter. However, at 20 wt.% of added thermoplastic the particles are the thermoplastic toughener in a continuous epoxy-rich phase, whilst at 35 wt.% of added thermoplastic phase inversion has occurred to give
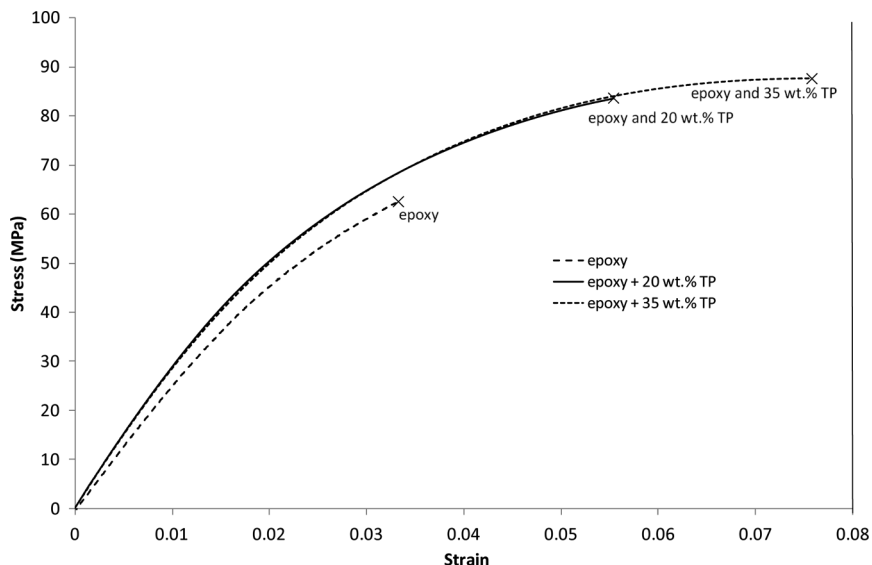
FIGURE 4 Engineering stress *versus* engineering strain curves for the epoxy polymer containing 0, 20, and 35 wt.% thermoplastic toughener.

particles of epoxy in a continuous thermoplastic-rich phase, *i.e.*, the poly(ether sulfone) copolymer.

3.3. Fracture Properties

The fracture toughness and fracture energy of the epoxy and epoxy/ thermoplastic blends were measured using compact-tension specimens. The results are shown in Table 3 which gives the complete set of fracture data, including values of the standard deviation (SD). Both the fracture toughness and the fracture energy increase with

TABLE 3 Fracture Results for Thermoplastic-Modified Epoxy Polymer

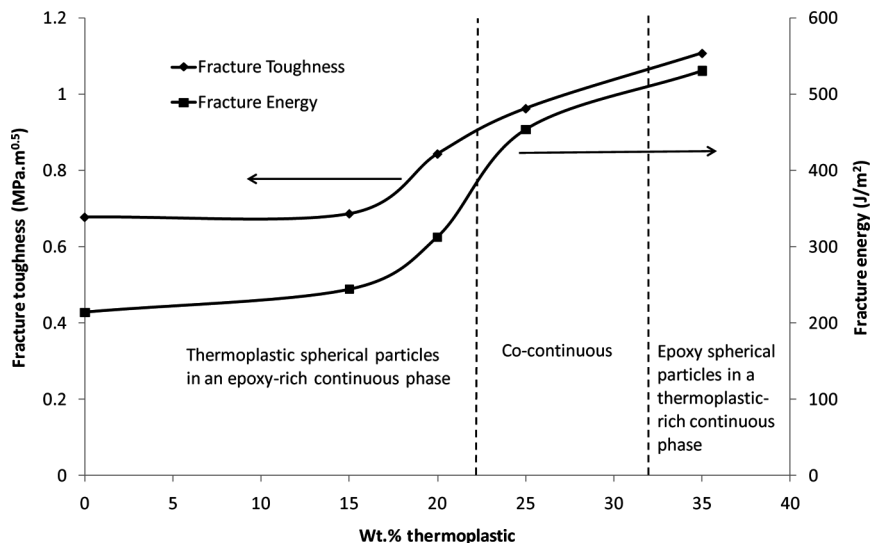| Thermoplastic content (wt.%)	Fracture toughness, K_{IC} (MPa·m$^{0.5}$)		Fracture energy, G_{IC} (J/m^2)	
	Mean	SD	Mean	SD
0	0.68	0.04	215	30
15	0.69	0.11	245	75
20	0.84	0.08	315	95
25	0.96	0.08	455	110
35	1.11	0.04	530	10

FIGURE 5 Fracture toughness and fracture energy as a function of the weight percentage of added thermoplastic toughener.

an increasing percentage of thermoplastic toughener. The pure epoxy has a fracture toughness of $0.68 \pm 0.04 \, \text{MPa} \cdot \text{m}^{0.5}$, which increased to $1.11 \pm 0.04 \, \text{MPa} \cdot \text{m}^{0.5}$ when $35 \, \text{wt.\%}$ thermoplastic was added. The fracture energy also increased from 215 ± 30 to $530 \pm 10 \, \text{J/m}^2$. From Fig. 5, it may be clearly seen that the increase in toughness is a steady progressive rise as a function of the added content of the thermoplastic toughener, *i.e.*, there is no sudden increase in the fracture properties which coincides with a change in morphology.

3.4. Toughening Mechanisms

The fracture surface of the unmodified epoxy was relatively smooth, flat, and featureless with only a few river lines visible in the SEM images, indicating a brittle failure.

The fracture surface of epoxy polymer containing $15 \, \text{wt.\%}$ of thermoplastic was examined using the atomic force microscope (AFM). (It should be noted that the fracture surfaces of samples containing $20 \, \text{wt.\%}$ or more of thermoplastic were too rough to be imaged successfully using the AFM.) The AFM images for the epoxy sample with $15 \, \text{wt.\%}$ thermoplastic revealed the spherical particulate morphology. However, during fracture it appears that the thermoplastic particles are plastically deformed, being drawn into peaks in the
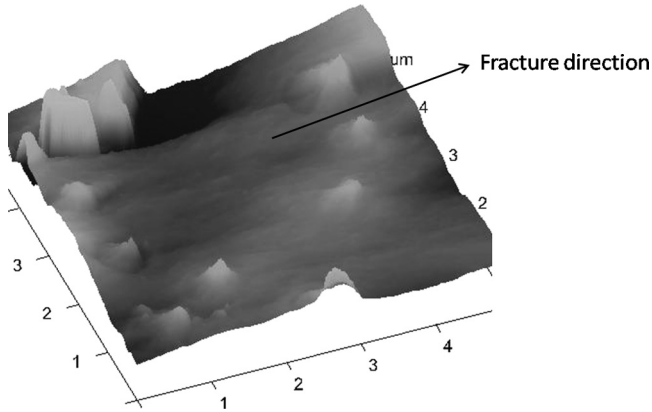
FIGURE 6 AFM image of the fracture surface of an epoxy polymer containing 15 wt.% of the thermoplastic toughener. The thermoplastic phase, in the form of spherical particles in an epoxy-rich continuous phase, has been drawn into peaks in the direction of crack growth.

direction of crack growth, as shown in Fig. 6. The height difference between these peaks and the surrounding epoxy is approximately 200 nm. When the material was cut, the height difference between the flat topped particles and the epoxy was only 10 nm, indicating that the thermoplastic is being drawn during fracture. The peaks within the thermoplastic particles can also be seen in the SEM images for samples containing 20 wt.% of thermoplastic, as shown in Fig. 7. This image not only shows the peaks formed by the plastically-deformed thermoplastic, but is also shows "tails" on the far side of the thermoplastic spheres. These tails are suggested to be where the crack has passed more slowly through the thermoplastic than it does through the epoxy, and the crack fronts meet up again on the far side of the thermoplastic particle at different levels. The effect of the crack front being at different levels gives rise to these tails [4]. This observed plastic deformation of the thermoplastic phase for the epoxy/thermoplastic blends containing 15 and 20 wt.% of the poly(ether sulfone) copolymer toughener will result in an increase in the fracture toughness and energy.

The more complex morphology seen for the 25 and 35 wt.% of added thermoplastic makes identifying the toughening mechanisms for these formulations more difficult, especially for the 25 wt.% sample for which SEM images were inconclusive. Notwithstanding, Fig. 8 shows an SEM image of the epoxy polymer containing 35 wt.% of the thermoplastic toughener. This content of the thermoplastic toughener
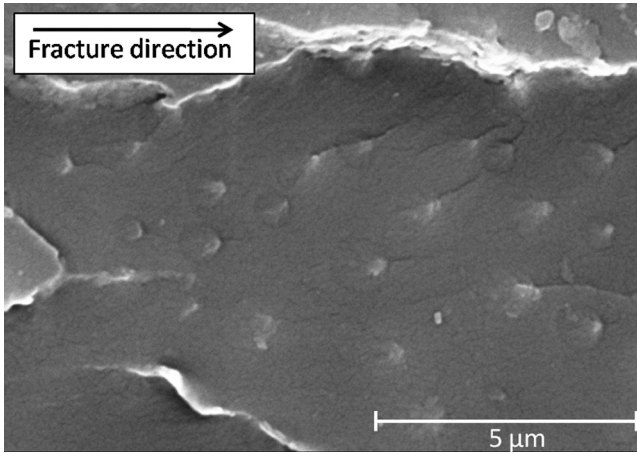
FIGURE 7 Scanning electron micrograph of the fracture surface of the epoxy polymer containing 20 wt.% thermoplastic toughener. The peaks in the thermoplastic spheres where the thermoplastic (in the form of spherical particles in an epoxy-rich continuous phase) has been plastically deformed, and the "tails" resulting from the crack fronts on the far side of the spheres being at different levels, may be seen.
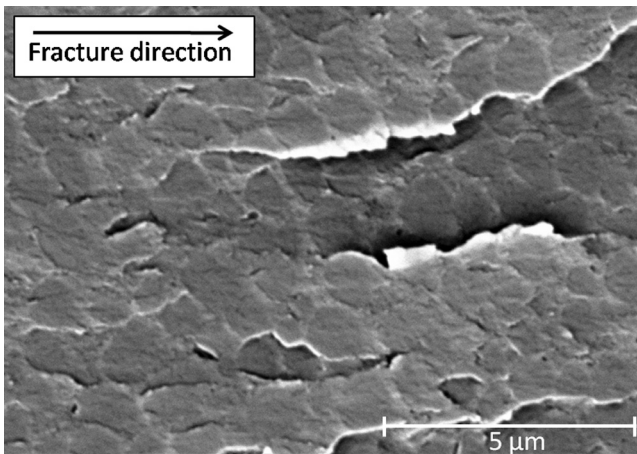

FIGURE 8 Scanning electron micrograph of the fracture surface of the epoxy polymer containing 35 wt.% of thermoplastic toughener, showing the phase-inverted microstructure of epoxy spherical particles in a thermoplastic-rich continuous phase, with the thermoplastic phase having been plastically deformed during testing.

gives rise to the phase-inverted morphology and the spherical epoxy particles can be seen within the thermoplastic-rich matrix. The thermoplastic appears as the light-coloured network which stands proud of the surface (the light colour for a secondary electron image indicates a high region), whereas the epoxy particles are darker (and hence lower). If a crack were to pass through such a two-phase material on a single plane then there would be no height differences between the phases and, hence, the phases would be very difficult to identify on a secondary electron image as they would show the same colour (greyscale). However, if the fracture were to pass through the material such that the fracture path was at different levels in the two phases (due to different properties between the epoxy and the thermoplastic), then statistically some of the thermoplastic would be higher than the epoxy and some would be lower. In this case some of the thermoplastic would appear darker than the epoxy particles. From Fig. 8 it is clear that there are no such dark areas of thermoplastic, showing that all of the thermoplastic is higher than the fractured epoxy spheres. This indicates that the thermoplastic has deformed during fracture.

To confirm this observation that plastic deformation of the thermoplastic phase had occurred, the fracture surface of this sample was heated to above the glass transition temperature of the thermoplastic. This caused a decrease in the brightness of this light-coloured thermoplastic network, although the magnitude of this decrease was small. This decrease shows that the thermoplastic has relaxed during reheating and, hence, confirms that it had been drawn during fracture. Note that plastic drawing of the thermoplastic was also observed for samples with 15 wt.% thermoplastic, as reported earlier.

Now, the thermoplastic and epoxy are far from fully phase-separated for samples containing either 25 or 35 wt.% thermoplastic, as discussed earlier, and it is possible that any epoxy that has been left in solution in the thermoplastic-rich phase has significantly chain-extended the thermoplastic polymer, which has reactive end-groups. This will lead to an increase in the molecular weight of the poly(ether sulfone) copolymer in the continuous thermoplastic-rich phase which, therefore, may well now possess a higher ductility; and, hence, the toughness of this formulation is increased. Kinloch *et al.* [2] reviewed the toughening mechanisms for epoxy and thermoplastic blends, covering cavitation of the thermoplastic and debonding of the thermoplastic from the epoxy. Neither of these mechanisms were seen in either this work or the work of Kinloch *et al.* However, Kinloch *et al.* concluded that chain extension of the poly(ether sulfone) could increase the toughness of the thermoplastic, and this could lead

to the toughening of the blend. This is the mechanism that is thought to result in the increase in toughness also seen in the work reported here, in addition to some plastic drawing of the thermoplastic phase that is also observed.

4. CONCLUSIONS

The work detailed in the present paper was undertaken to investigate how a thermoplastic polymeric additive might toughen an epoxy polymer, without reducing its thermal stability or Young's modulus. The epoxy used was a blend of a diglycidyl ether of bisphenol F and a triglycidyl aminophenol crosslinked with an amine curing agent. The epoxy polymer had a glass transition temperature of about 200°C. The thermoplastic toughener was a reactively terminated poly(ether sulfone) copolymer and was added at various concentrations between 15 and 35 wt.%. The thermoplastic toughener had a similar glass transition temperature to the epoxy polymer. The different contents of thermoplastic toughener gave rise to a range of morphologies from spherical particulate, through co-continuous, to phase inverted. The addition of the reactively terminated poly(ether sulfone) copolymer thermoplastic was found to have no major effect on the Young's modulus of the epoxy polymer. It did, however, increase the ultimate tensile strength and the strain to break of the epoxy polymers, as measured from uniaxial tensile tests. More importantly, the addition of the thermoplastic toughener increased the fracture toughness and fracture energy of the epoxy polymer. The fracture toughness increased from $0.68\,\mathrm{MPa\cdot m^{0.5}}$ for the unmodified epoxy to $1.11\,\mathrm{MPa\cdot m^{0.5}}$ at 35 wt.% of added thermoplastic, and the fracture energy rose from 215 to $530\,\mathrm{J/m^2}$. The increase in the fracture properties, when plotted as a function of the content of added thermoplastic toughener, revealed no sudden step changes associated with changes in morphology. Indeed, the increase in toughness was a steady progressive rise as a function of the added content of the reactively terminated poly(ether sulfone) copolymer toughener. The operative toughening mechanism was suggested to be plastic deformation of the thermoplastic-rich phase, which enhances the overall toughness of the thermoplastic-toughened epoxy polymer.

ACKNOWLEDGMENTS

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