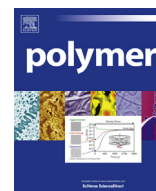




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Improving the fracture toughness and the cyclic-fatigue resistance of epoxy-polymer blends

A.J. Kinloch^{*}, S.H. Lee, A.C. Taylor^{*}

Imperial College London, Department of Mechanical Engineering, South Kensington Campus, London SW7 2AZ, UK

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ABSTRACT

Relatively tough epoxy-blend polymers are now commercially available for use as adhesives and as the matrices for fibre composites. Nevertheless, another failure property which may be of equal, or even of greater, importance in some applications is the resistance of the epoxy polymer to cyclic-fatigue loading. However, the cyclic-fatigue behaviour of epoxy polymers has not been studied in great detail, especially for epoxy polymers where the material has been modified by forming a polymer blend in order to increase its toughness under quasi-static test rates or impact test rates. Therefore, a major aim of the present work has been to undertake a novel investigation of a range of rubber and thermoplastic materials to modify an epoxy polymer to study whether both a relatively high toughness and a significantly improved cyclic-fatigue behaviour can be simultaneously achieved in a given formulation. The unmodified epoxy-polymer possessed a value of the fracture energy, G_{IC} , of 495 J/m² and a value for the threshold value of the maximum strain-energy release rate in a fatigue cycle, G_{th} , (below which no significant crack growth occurs) of 155 J/m². Several epoxy-polymer blends have been identified which do show major increases in these values and probably the best combination of such properties were for the epoxy-polymers modified with a poly(propylene-glycol)-based polyurethane (PU) modifier: either when used by itself or as a 'hybrid' polymer-blend in combination with core-shell rubber (CSii) particles, based upon a styrene-butadiene rubber core. For these PU-based epoxy polymers the values of G_{IC} and G_{th} were found to increase to values of about 2475 J/m² and 445 J/m², respectively. The mechanisms of toughening that were induced by the addition of the polymer-blend modifier revealed that the presence of a multiphase in the epoxy-blend polymer was a critical requirement in achieving relatively high values of G_{IC} and G_{th} . This was due to the second-phase particles initiating plastic deformation of the epoxy-matrix phase, which was the major source of energy dissipation and toughening. In turn, the extent of energy dissipated by the plastic deformation of the epoxy-matrix phase is clearly greatly influenced by the degree of ductility exhibited by this phase of the epoxy-blend polymer. Thus, another important feature of the degree of toughening observed is the effect that the modifier has upon the yield stress and plastic failure strain of the epoxy-matrix phase.

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1. Introduction

Thermosetting epoxy polymers are widely used as engineering adhesives and matrices for fibre-composite materials. When cured, epoxy polymers typically possess a high crosslink density. This property leads to good thermal stability and creep resistance, relatively high modulus, and excellent adhesion properties of the crosslinked epoxy polymer. Unfortunately, the high crosslink

density also leads to low ductility and poor fracture toughness, which limits their application as engineering materials.

A very successful route to improving the toughness of thermosetting polymers is to form a blend of the epoxy resin with a low molecular-weight rubber, where the rubber undergoes polymerisation and phase-separation upon curing the blend [1–4] to give a multiphase microstructure. The rubber-modified epoxy-polymer often possesses outstanding fracture properties. Many different mechanisms have been proposed to explain the greatly improved fracture toughness that may result when an epoxy polymer possesses a multiphase microstructure of dispersed rubber particles. Much of the dispute has concerned whether the rubber particles or the epoxy-matrix phase absorbs most of the energy. However, it is

^{*} Corresponding authors.

E-mail addresses: a.kinloch@imperial.ac.uk (A.J. Kinloch), a.c.taylor@imperial.ac.uk (A.C. Taylor).

now well established [5–7] that plastic deformation of the epoxy-matrix phase is the main source of energy dissipation and increased toughness. Such enhanced plastic deformation arises from the interactions of the triaxial stress-field ahead of a crack tip and the rubber particles. The stress-field associated with the rubber particles leads to the initiation of two important deformation processes that can strongly interact. One such process is the initiation and growth of multiple localised shear-yield deformations in the epoxy-matrix phase, since the stress concentrations around the rubber particles act as initiation sites for such plastic-shear deformation. Because there are many such particles, considerably more plastic deformation occurs in the multiphase epoxy-blend than in the unmodified material. However, the plastic deformation is localised to form plastic-shear bands through (a) the post-yield strain-softening of the epoxy-matrix phase, and (b) the fact that shear deformations initiate at one particle but terminate at another. The other important deformation process involves cavitation of the rubber particles. The importance of the formation of such voids in the rubber particles ahead of the crack tip is not due to the energy that is associated with the formation of these voids. The energy dissipation associated with this phenomenon is typically of little significance [8]. Rather, it is the fact that the formation of these voids enables further plastic deformation in the epoxy-matrix phase to develop. This arises from two aspects. Firstly, the presence of the voids in the rubber particles lowers the extent of stress triaxiality in the adjacent matrix, which reduces the stress required for shear yielding and so promotes more localised plastic-shear deformations in the epoxy-matrix phase of the type described above. Secondly, the formation of the voids in the rubber particles enables plastic void, i.e. hole, growth in the epoxy-matrix phase to occur.

More recently, the introduction of rubber particles in the epoxy polymer has also been achieved via the addition of preformed core-shell rubber particles. These particles consist of a soft rubber core within a harder shell. The particles are typically formed by emulsion polymerisation and are then dispersed in the epoxy resin which is then cured. Hence, it is readily possible to produce particles with a controlled particle size, unlike with phase-separating rubbers. A range of core and shell materials may be used, and multilayer particles are common [9–12]. The shell is chosen to be compatible with the epoxy polymer, and poly(methyl methacrylate), which is sometimes functionalised, is often used. Typical rubber-core materials include polybutadiene [10], acrylate-polyurethane rubbers [11] and polysiloxane rubbers [12]. The toughening mechanisms in these epoxy-polymer blends have been found to be very similar to those discussed above for the modified epoxy-polymers which contain rubber particles produced via a phase-separation route.

Indeed, the basic toughening mechanisms discussed above have also been shown to be operative when the epoxy polymer is modified via the inclusion of nano-silica particles. Such modified epoxy-polymers have typically been created during a sol-gel manufacturing process [13]. Here the silica particles are formed *in-situ*, and the particle size of 20 nm and the excellent dispersion of these SiO₂ particles remained unchanged during any further mixing or curing operations. However, in the case of these nano-silica particles they cannot, of course, undergo internal cavitation in the triaxial stress-field ahead of the crack tip but debond instead to create the 'initial void', which then enables plastic void growth of the epoxy polymer to occur. Finally, it was also found that, whilst the presence of nano-silica particles could offer significant improvements in several key properties, the increases in toughness that they could impart to an epoxy polymer was significantly inferior to that typically seen in rubber-modified epoxy-polymers [14,15].

Yet another approach to toughening epoxy polymers is based upon blending the epoxy with a thermoplastic polymer, or oligomer, that phase-separates upon curing of the resin [16–30]. The thermoplastics employed have typically been functionalised poly(ether sulfone) [17,20–23], poly(ether imide) [18,24,25], polyimide [26], polysulfone [27,28], polyester [22], syndiotactic polystyrene [29] and diblock copolymers such as poly(ethylene-propylene)-*b*-(polyethylene oxide) [30]. For these thermoplastic-modified epoxy-polymers, in addition to the above toughening mechanisms which may be operative, there is also the possibility that plastic deformation of a relatively ductile thermoplastic-polymer phase may occur and so contribute significantly to an increase in the toughness.

Now, the above discussions have focused on increasing the toughness, and the toughening mechanisms, of modified epoxy-polymers under a constant rate of testing (e.g. quasi-static or impact test-rates) and, as can be appreciated from the above discussions, this topic has received much industrial and academic attention in recent years. Indeed, relatively tough epoxy-blend polymers for use as adhesives and as the matrices in fibre composites are now commercially available. Nevertheless, another failure property which may be of equal, or even of greater, importance in some applications is the resistance of the epoxy polymer to cyclic-fatigue loading. However, the cyclic-fatigue behaviour of epoxy polymers has not been studied in great detail, especially for epoxy-blend polymers where the material has been modified in order to increase its basic toughness under quasi-static or impact test-rates. Therefore, a major aim of the present work is to undertake a novel investigation of a range of rubber and thermoplastic materials to modify an epoxy polymer to study whether both a relatively high toughness and a significantly improved cyclic-fatigue behaviour can be simultaneously achieved in a given epoxy-blend formulation.

2. Experimental studies

2.1. Materials

The thermosetting polymers were based upon a single-component hot-cured epoxy and were formulated by Henkel, Dusseldorf, Germany. The epoxy resin was a standard diglycidyl ether of bis-phenol A (DGEBA), with an epoxide equivalent weight (EEW) of 188 g/eq, and was crosslinked using dicyandiamide as the curing agent. To accelerate the curing reaction fenuron was employed, and an epoxy reactive diluent and a thixotrope, i.e. fumed silica, were used to give a viscosity suitable for producing cast sheets. The formulation for the unmodified, i.e. control, epoxy-polymer is shown in Table 1. It should be noted that the epoxy resin and the curing agent were always mixed at a weight ratio of 93:10. When a given concentration of the modifier, see below, was added to this unmodified-epoxy formulation, then the equivalent amount of the epoxy-dicyandiamide mixture was omitted. Thus, the weight percentage of the thixotrope, diluent and accelerator were unchanged and the sum of the weight percentages of the epoxy resin, curing agent and modifier was always 92.5 wt.%.

Table 1
Unmodified epoxy formulation.

Constituent	Chemical type	Weight %
Epoxy resin	DGEBA	83.5
Curing agent	Dicyandiamide	9.0
Thixotrope	Fumed silica	3.5
Diluent	Epoxy reactive diluent	3.5
Accelerator	Fenuron	0.5

Table 2

Details of the simple polymeric-modifiers employed.

Modifier	Name	M_w (g/mol)	T_g (°C)
A difunctional epoxydised polysulfide	PS	1200	–30
A 46 w/w% of a chain-extended and epoxy-terminated poly(propylene glycol) in an epoxy-dicyandiamide masterbatch	PPGm	5000–10,000	5
A poly(propylene glycol)-based polyurethane	PU	10,000–20,000	–42

Notes: M_w : weight-average molecular-weight; T_g : glass transition temperature.

The unmodified, i.e. 'control', epoxy-polymer was modified by the addition of (a) simple polymeric-modifiers and (b) core-shell rubber particles. Further, the use of 'hybrid' modifiers, where the unmodified epoxy-polymer was blended with two different modifiers in order to try to achieve both excellent toughness and fatigue resistance was studied. The details of the simple polymeric-modifiers and core-shell rubber particles employed in the present work are given in Tables 2 and 3 respectively. The various formulations employed are listed in Table 4.

Cast sheets of the various epoxy polymers were prepared in a steel picture-frame mould. The surfaces of the mould were first coated with a release agent ('Frekote 700-NC', Loctite, Germany). The cartridge of the epoxy-resin formulation was taken from the freezer and defrosted at 65 °C for 45 min and then pumped into the steel mould. Before closing the mould, the epoxy was degassed in a vacuum oven at 65 °C for 30 min. The closed mould was then placed in an oven which was heated to 85 °C at a heating rate of 0.5 °C/min and was then held at 85 °C for a further 60 min. The temperature of the oven was then raised to 100 °C at a heating rate of 0.1 °C/min and, when the temperature of 100 °C was reached, the temperature was raised to 183 °C at a heating rate of 1 °C/min and this temperature was maintained for a further 70 min. The temperature of the epoxy formulation in the steel mould was measured using thermocouples and was in very good agreement with the temperature recorded in the oven. This rather complex curing schedule was developed in order to ensure that the epoxy formulation was fully cured, but without causing an exothermic reaction and hence a drastic temperature rise of the curing epoxy.

2.2. Microstructure and thermal studies

Atomic force microscopy (AFM) studies were undertaken using a 'MultiMode' scanning probe microscope from Veeco, UK, equipped with a 'NanoScope IV' controlled 'J-scanner'. A smooth surface was first prepared by cutting samples of the cured plates of epoxy polymers, employing a 'PowerTome XL' cryo-ultramicrotome from RMC Products, UK, at temperatures down to –100 °C. Then AFM scans were performed in the tapping mode using a silicon probe with a 5 nm tip, and both height and phase images were recorded.

Dynamic mechanical thermal analysis (DMTA) was used to measure the glass transition temperature, T_g , of the cured formulations. A beam of $3 \times 10 \times 60$ mm³ was cut from the cured plates and tested using a 'DMTA Q800' (TA Instruments, Delaware, USA) machine. The clamped specimen was oscillated at a frequency of 1 Hz with a 20 µm deflection. The test temperature was varied from –100 °C to 250 °C at a heating rate of 4 °C/min. The typical

Table 3

Details of the core-shell rubber-particle modifiers employed.

Core	Shell	Name	Diameter (nm)	Core T_g (°C)
Polybutadiene	f-PMMA	CSi	100	–85
Styrene-butadiene rubber	f-PMMA	CSii	100	–55

Notes: f-PMMA: functionalised poly(methyl methacrylate).

variation in replicate results gave a value of T_g accurate to about ± 1 –2 °C.

2.3. Modulus and yield behaviour studies

Uniaxial tensile tests were conducted on the epoxy polymers in accordance with ISO 527 [31,32]. Tensile dumbbells were machined from the cured plates and were tested at a displacement rate of 1 mm/min, and the displacement in the gauge length was measured using an extensometer. The tensile Young's modulus, E , was ascertained.

The overall yield behaviour was ascertained using plane-strain compression tests, since the epoxy polymers failed at around the yield point when the uniaxial tensile tests were undertaken. The plane-strain compression tests were conducted as described by Williams and Ford [33]. Tests were conducted using $3 \times 40 \times 40$ mm³ specimens loaded in compression between two parallel, 12 mm wide, platens at a constant displacement rate of 0.1 mm/min, and the results were corrected for the compliance of the test machine and test rig. The yield stress, σ_{yc} , was defined as the first locus of the true stress-true strain curve with a zero gradient. The true tensile yield stress, σ_{yt} , was then calculated from the values of σ_{yc} [34].

Optical cross-sections were cut from the compressed region and polished using a 'Labopol-21' from Struers, UK. They were then polished employing progressively finer grades of emery paper up to 4000 grit, which is equivalent to a 3 µm polishing powder. The samples were bonded onto standard glass microscope slides using an optically-transparent, room-temperature curing, epoxy, 'Araldite 2020' from Huntsman, UK, and were finally polished to a nominal thickness of approximately 100 µm. The cross-sections were observed using transmission optical microscopy between crossed polarisers, using an 'Axioscope A1' microscope from Carl Zeiss, UK.

2.4. Fracture studies

Single-edge notch-bend (SENB) tests were conducted in accordance with ISO 13586 [35] to obtain values for the plane-strain initiation fracture energy, G_{Ic} , and fracture toughness, K_{Ic} , of the epoxy polymers. To obtain sharp cracks, the tips of the initial machine-notch in the SENB specimens were tapped using a cooled razor blade. Crack lengths of the order of $a/w = 0.5$ were obtained, where a is the crack length and w is the width of the test specimen, and the thickness, B , of the SENB specimens was 7 mm. The fracture energy, G_{Ic} , was calculated using the energy method, and the fracture toughness was calculated using the fracture load. As a cross-check, the fracture energy for each material was also calculated from the measured values of K_{Ic} and the tensile modulus, E ; and very good agreement between the values was found. The standard deviation in the value of G_{Ic} from the replicate tests is represented by the error bars shown later in Fig. 2.

2.5. Cyclic-fatigue studies

The bulk sheets of the epoxy formulations were machined to produce compact-tension specimens [35] for cyclic-fatigue testing [36]. Again, a natural crack was generated by tapping a cooled razor-blade into the machined notch. The fatigue tests were conducted in displacement control, with a displacement ratio, $\delta_{min}/\delta_{max}$, of 0.5. Sinusoidal loading was used, with a frequency of 5 Hz. The rate of cyclic-fatigue growth per cycle, da/dN , was measured as a function of the maximum strain-energy release-rate, G_{max} , applied in a fatigue cycle. The former parameter, da/dN , was determined via using both a crack-gauge electrical-transducer

Table 4
Thermal and mechanical properties of the various epoxy formulations.

Name of formulation	T_g (°C)	SD ($\pm$ °C)	E (GPa)	SD ($\pm$ GPa)	σ_{yt} (MPa)	SD ($\pm$ MPa)	ϵ_{fc} (%)	SD ($\pm$ %)	G_{lc} (J/m ²)	SD ($\pm$ J/m ²)	G_{th} (J/m ²)	SD ($\pm$ J/m ²)
Unmodified	132	1	3.53	0.09	93	3	85	4	495	80	155	10
Simple polymeric-modifiers:												
10PS	105	2	3.42	0.05	92	1	99	5	560	80	110	5
10PPGm	116	2	3.31	0.06	77	1	92	5	890	40	155	10
10PU	125	2	2.72	0.01	70	2	104	6	2380	230	445	20
Core-shell rubber modifiers:												
10CSi	134	1	2.63	0.07	71	1	88	4	1940	180	125	10
10CSii	129	1	2.61	0.06	68	1	97	5	2540	220	195	15
'Hybrid' modifiers:												
10PS + 10CSii	104	2	2.88	0.05	64	1	93	5	1650	60	150	10
10PPGm + 10CSi	116	2	2.56	0.11	76	4	102	5	2830	285	330	30
10PPGm + 10CSii	116	2	2.55	0.05	58	2	114	6	1820	260	300	20
10PU + 10CSii	120	2	2.41	0.12	55	2	122	6	2570	190	440	40
Optimised 'hybrid' modifiers:												
20PS + 15CSii	77	2	2.45	0.03	52	2	143	7	2970	240	300	15

Notes: The number given in the first column indicates the percentage by weight of that modifier used in the epoxy formulation; SD: standard deviation.

system from Rumul, Schaffhausen, Switzerland and visual measurements using a travelling microscope. The results from these two very different techniques were found to be in excellent agreement. Of special importance was the determination of the threshold value, G_{th} , of the maximum value of the applied strain-energy release-rate below which no significant fatigue crack growth occurs. The standard deviation in the value of G_{th} from the replicate tests is represented by the error bars shown later in Fig. 2.

2.6. Fractographic studies

The fracture surfaces of the epoxy polymers were studied using high-resolution scanning electron-microscopy. This was performed using a scanning electron microscope (SEM) equipped with a field-emission gun (FEG-SEM). A Carl Zeiss, Germany, 'Leo 1525' with a 'Gemini' column was used with a typical accelerating voltage of 5 kV. All specimens were coated with an approximately 5 nm thick layer of chromium before imaging. The resulting FEG-SEM micrographs were used in order to deduce the mechanisms responsible for any improvements in the quasi-static toughness or the cyclic-fatigue behaviour for the modified epoxy-polymers. For the latter fatigue tests, the fracture surfaces were examined in the region of the compact-tension specimen where the threshold value, G_{th} , was determined. It should be noted that analysis of the toughening mechanisms in the present materials is somewhat complicated by

the presence of the fumed silica. Since the fumed silica can debond from the epoxy leading to some void growth and plastic deformation of the epoxy, and hence to an small increase in the toughness compared to a formulation of the unmodified epoxy-polymer containing no fumed silica. However, generally the fumed silica behaved in a similar manner for all of the formulations, and so its effects could be readily disregarded.

3. Results and discussions

3.1. Introduction

The unmodified, i.e. 'control', epoxy-polymer will be discussed first, followed by this epoxy polymer being modified by the addition of simple polymeric-modifiers and then by core-shell rubber particles. In the final section, the use of 'hybrid' modifiers, where the unmodified epoxy-polymer was blended with two different modifiers in order to try to achieve both excellent toughness and fatigue resistance will be considered. The results from the various studies are shown in Table 4, together with their respective standard deviations.

3.2. Unmodified epoxy-polymer

The main properties of the unmodified epoxy are shown in Table 4. The glass transition temperature, T_g , was 132 °C and a β -relaxation was also observed at −68 °C. As discussed above, the

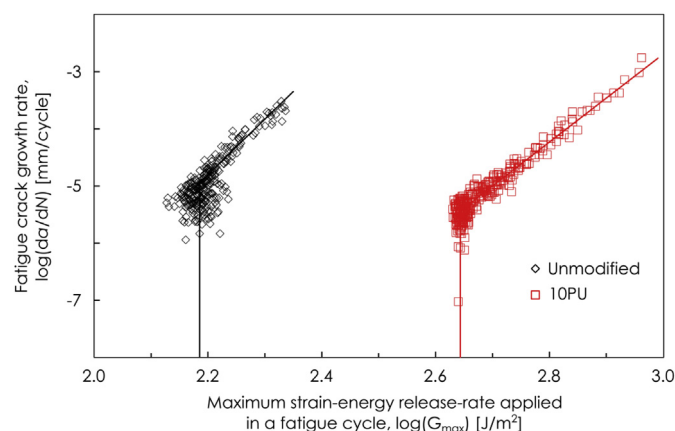


Fig. 1. The rate of cyclic-fatigue growth per cycle, da/dN , as a function of the maximum strain-energy release-rate, G_{max} , applied in a fatigue cycle for the unmodified epoxy-polymer and '10PU epoxy-polymer'.

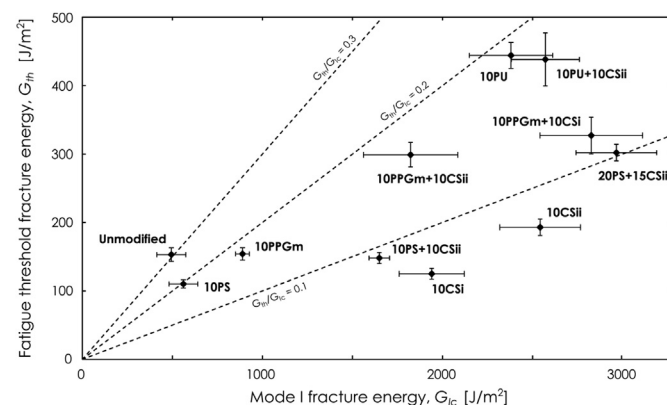


Fig. 2. Quasi-static fracture and cyclic-fatigue properties for the unmodified and modified epoxy-polymers.

unmodified, 'control' formulation was a DGEBA epoxy resin containing a reactive diluent, fenuron, dicyandiamide and fumed silica. The atomic force microscopy (AFM) and scanning electron microscopy (SEM) images revealed that, when cured, the unmodified epoxy-polymer was homogeneous except for the presence of aggregates of fumed silica. As reported previously [37], these aggregates consisted of chain-like structures which aggregated together to give spherical particles with a diameter of about $30 \pm 10 \mu\text{m}$.

The Young's modulus, E , of the unmodified epoxy polymer was 3.53 GPa and the true tensile yield stress, σ_{yt} , was 93 MPa and was calculated via measuring the compressive yield stress, as described above. The compressive failure strain, ϵ_{fc} , was 85% and again was measured using the plane-strain compression test. The value of the fracture energy, G_{Ic} , was as expected relatively low with a value of 495 J/m^2 . The measured data for the rate of cyclic-fatigue growth per cycle, da/dN , as a function of the maximum strain-energy release-rate, G_{max} , applied in a fatigue cycle for the unmodified epoxy-polymer is shown in Fig. 1. As may be seen, the threshold value of the maximum strain-energy release-rate, G_{th} , applied in a fatigue cycle, below which no significant fatigue crack growth occurs, may be defined and the value of the cyclic-fatigue threshold fracture energy, G_{th} , was 155 J/m^2 .

Fig. 2 shows graphically the relationship between the values of the fatigue threshold fracture energy, G_{th} , and the fracture energy, G_{Ic} , for the unmodified epoxy-polymer. The point on Fig. 2 for the unmodified epoxy-polymer acts, of course, as the reference point for the modified epoxy-polymers which have been formulated with the aim of increasing not only the toughness, G_{Ic} , but also the cyclic-fatigue behaviour via increasing the value of G_{th} . Also, three dashed lines are shown on Fig. 2 with the intention of guiding the reader's attention to three values of the ratio G_{th}/G_{Ic} ; since an aim of the present study is to achieve a relatively high value of this ratio G_{th}/G_{Ic} , whilst attempting to also obtain a relatively high absolute value of G_{Ic} .

3.3. Simple polymeric-modifiers

3.3.1. Introduction

The simple polymeric-modifiers studied were (a) a difunctional epoxydised polysulfide (PS), (b) a chain-extended and epoxy-terminated poly(propylene glycol) modifier in an epoxy/dicyandiamide masterbatch (PPGm), and (c) a poly(propylene glycol)-based polyurethane (PU). The basic properties of these modifiers are given in Table 2 and they were all used at a concentration of 10 wt.% of the modifier in the unmodified epoxy-polymer.

3.3.2. Microstructural studies

The T_g of the epoxy polymer modified with 10 wt.% of the PS modifier (termed '10PS epoxy-polymer') was 105°C . Thus, the T_g of this modified epoxy-polymer is significantly lower than that of the unmodified epoxy, which indicates that the PS modifier is soluble in the epoxy. Now, the Fox equation [38] may be used to predict the degree of solubility of the modifier in the epoxy polymer, due to the decrease observed in the value of the T_g of the epoxy polymer. The T_{gs} of the PS modifier and the pure epoxy-polymer were -30°C and 132°C , see Tables 2 and 4, respectively. Hence, the decrease in the T_g of the '10PS epoxy-polymer' to 105°C , from 132°C , leads to the prediction that all of the PS modifier that was added to the formulation dissolved and remained in solution in the cured epoxy-polymer. This prediction was confirmed from the AFM studies which revealed that the morphology of the '10PS epoxy-polymer' was identical to that of the unmodified epoxy, i.e. with no multi-phase microstructure being apparent.

The T_g of the epoxy polymer modified with 10 wt.% of the PPGm modifier (termed '10PPGm epoxy-polymer') was 116°C . Thus, the

T_g of this modified epoxy-polymer is again significantly lower than that of the unmodified epoxy, which indicates that the PPGm modifier is soluble in the epoxy-matrix phase. Indeed, when the Fox equation [38] was used, with the T_{gs} of the pure epoxy-polymer of 132°C and the PPGm modifier of 5°C , then the decrease in the T_g to 116°C for the '10PPGm epoxy-polymer' leads to the prediction that about 85 wt.% of the PPGm modifier that was added to the formulation had dissolved and remained in solution in the cured epoxy-matrix phase. This prediction was confirmed from the AFM studies which revealed that in the case of the '10PPGm epoxy-polymer' a second polymer-blend phase was indeed present. This phase was 'worm-like' in appearance with a length of about 100 nm and a width of 10 nm, see Fig. 3.

The T_g of the epoxy polymer modified with 10 wt.% of the PU modifier (termed '10PU epoxy-polymer') was 125°C . Thus, the T_g of this modified epoxy-polymer is somewhat lower than that of the unmodified epoxy, which indicates that the PU modifier is again soluble to some extent in the epoxy-matrix phase. Indeed, when the Fox equation [38] was used with the T_{gs} of the pure epoxy-polymer of 132°C and the PU modifier of -42°C , then the decrease in the T_g for the '10PU epoxy-polymer' to 125°C leads to the prediction that about 20 wt.% of the PU modifier that was added to the formulation had dissolved and remained in solution in the cured epoxy-matrix phase. This prediction was confirmed from the AFM studies which revealed that in the case of the '10PPU epoxy-polymer' a second polymer-blend phase was indeed present. As for the '10PPGm epoxy-polymer' shown in Fig. 3, this phase was 'worm-like' in appearance and had a length of about 90 nm and a width of 10 nm.

3.3.3. Mechanical properties

The mechanical properties are given in Table 4. The values of the modulus, E , and the true tensile yield stress, σ_{yt} , for the modified epoxy-polymers are decreased somewhat when the 10PS and 10PPGm modifiers are employed but undergo a more significant decrease upon the addition of the 10PU modifier. On the other hand, the compressive failure strain, ϵ_{fc} , was found to be slightly higher for the '10PU epoxy-polymer', compared to the unmodified

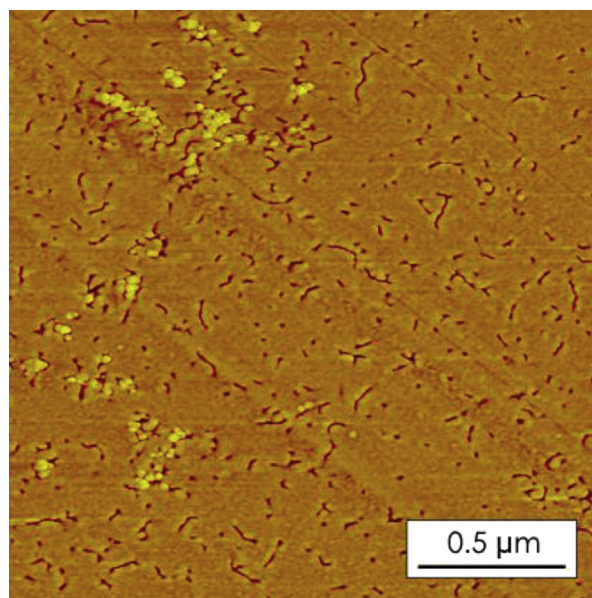


Fig. 3. AFM micrograph of the '10PPGm epoxy-polymer' showing the worm-like nature of the second phase of the PPGm particles. (A few aggregates of fumed-silica may also be seen.)

epoxy-polymer and when the 10PS and 10PPGm modifiers were employed.

The values of the fracture energy, G_{Ic} , for the '10PS epoxy-polymer' and the '10PPGm epoxy-polymer' are somewhat greater than that of the unmodified epoxy polymer, see Table 4. On the other hand, the value of G_{Ic} for the '10PU epoxy polymer' demonstrates a major increase compared to the unmodified epoxy polymer. Namely, for the '10PU epoxy-polymer' the value of G_{Ic} is 2380 J/m^2 , which may be compared to the value of 495 J/m^2 for the unmodified epoxy.

A similar observation may be made with respect to the values of the cyclic-fatigue threshold fracture energy, G_{th} . Firstly, when the 10PS and 10PPGm modifiers were employed there was no significant increase in the value of G_{th} , compared to the unmodified epoxy-polymer. However, the '10PU epoxy-polymer' showed a major increase to 445 J/m^2 , compared to the value of 155 J/m^2 for the unmodified epoxy-polymer. The measured data for the rate of cyclic-fatigue growth per cycle, da/dN , as a function of the maximum strain-energy release-rate, G_{max} , applied in a fatigue cycle for the '10PU epoxy-polymer' is shown in Fig. 1. As may be seen, the threshold value of the maximum strain-energy release-rate, G_{th} , applied in a fatigue cycle, below which no significant fatigue crack growth occurs, may be readily defined.

A plot of the cyclic-fatigue threshold fracture energy, G_{th} , versus the fracture energy, G_{Ic} , for these various epoxy-blend polymers is shown in Fig. 2. This graph clearly confirms that the 10PS and 10PPGm modifiers do not have any major effect on the quasi-static toughness, nor on the cyclic-fatigue behaviour of the epoxy polymer. However, the addition of the PU modifier at 10 wt.% is very significant, with respect to increasing greatly the values of both G_{th} and G_{Ic} , compared to the unmodified epoxy-polymer.

3.3.4. Toughening mechanisms

For the '10PS epoxy-polymer', the polysulfide remained in solution in the epoxy polymer and hence only a single-phase microstructure was observed. This led to a decrease in the measured T_g , but the yield stress was not significantly reduced. Hence, no additional toughening mechanisms were initiated, and there was no significant difference between the measured fracture energy and that of the unmodified polymer. Polarised optical microscopy showed that shear banding did occur, see Fig. 4. However, shear banding was also observed for the unmodified epoxy-polymer, and the '10PS epoxy-polymer' shows no significant difference in the extent of shear banding and hence no additional toughness.

For the '10PPGm epoxy-polymer', the fracture surfaces showed that the worm-like PPGm nanoparticles debonded from the epoxy, but there was no noticeable void growth. However, the yield stress was reduced by the presence of the PPGm and significant strain-softening was observed from the measured compressive stress-versus strain curve. Shear banding was also observed to occur, see Fig. 4, and these shear bands are less diffuse than for the unmodified epoxy and the '10PS epoxy-polymer'. These factors led to a relatively modest increase in the fracture energy, G_{Ic} , to 890 J/m^2 for the '10PPGm epoxy-polymer'. Under cyclic-fatigue loading, the '10PS epoxy-polymer' and the '10PPGm epoxy-polymer' both showed no increase in the measured threshold, G_{th} , compared to the unmodified epoxy, and no additional toughening mechanisms were visible on the fracture surfaces of the specimens which had been subjected to cyclic-fatigue testing.

For the '10PU epoxy-polymer', the PU particles, which were about 90 nm long, were seen to debond from the epoxy to form voids which then grew in size via plastic deformation of the epoxy-matrix phase, see Fig. 5. As commented above, this mechanism was

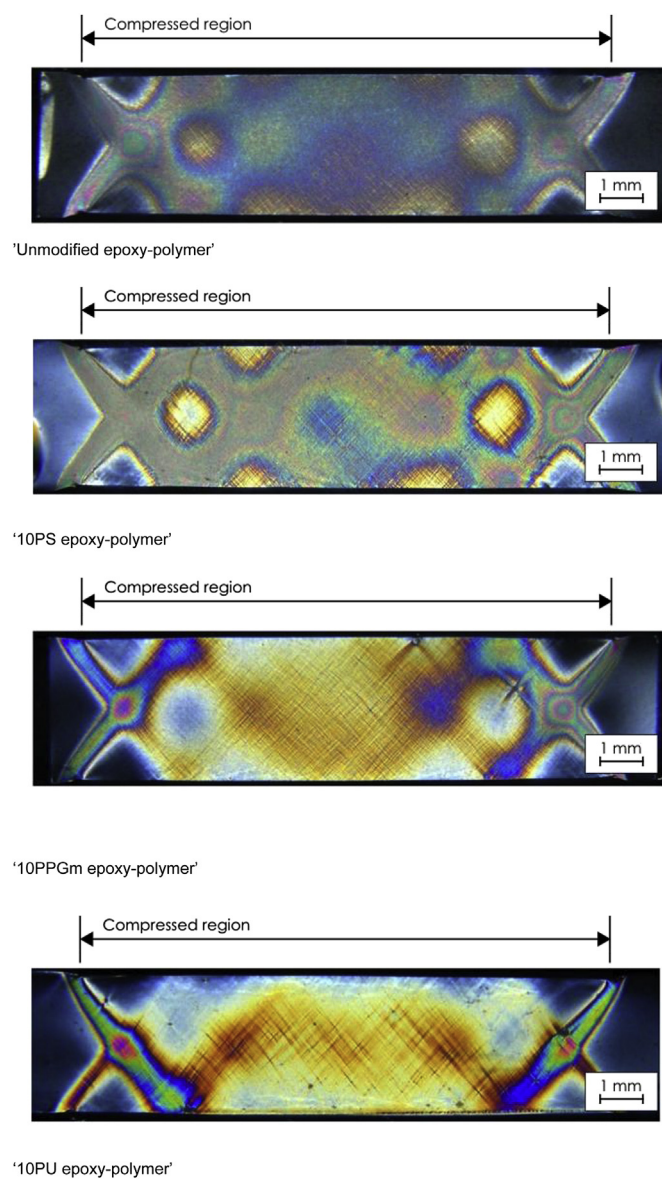


Fig. 4. Cross-sections of plane-strain compression specimens examined using cross-polarised transmission optical microscopy.

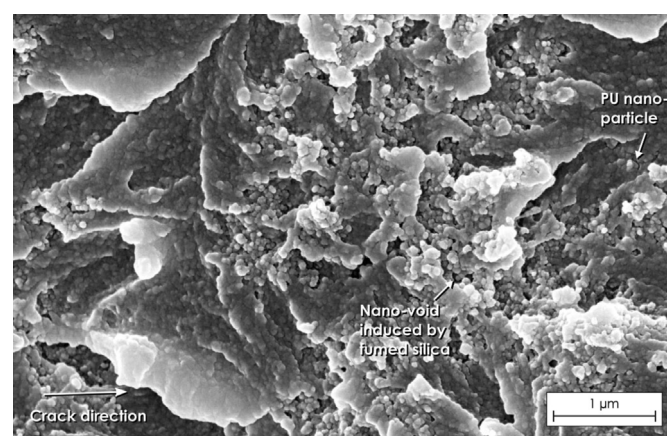


Fig. 5. SEM micrograph of the quasi-static fracture surface of the '10PU epoxy-polymer'. (The fumed silica aggregates and the debonded polyurethane particles are indicated on the figure.)

not observed for either of the other simple polymeric-modifiers. A significant extent of shear banding was also observed to occur for '10PU epoxy-polymer', see Fig. 4. Further, the reduced yield stress and increased strain to failure of the '10PU epoxy-polymer', see Table 4, obviously reflects an increase in the ductility of the epoxy-matrix phase. All these factors appear to have combined to give a significant toughening effect, with a value of G_{IC} of 2380 J/m² being measured for the '10PU epoxy-polymer'. Similar toughening mechanisms, but to a lesser extent, were also observed under cyclic-fatigue loading and led to an increase in the value of G_{th} . Indeed, a value of 445 J/m² was measured for the '10PU epoxy-polymer', compared to 155 J/m² for the unmodified epoxy-polymer. The very good fracture and fatigue performance of the '10PU epoxy-polymer' may be readily seen from Fig. 2.

3.4. Core-shell rubber modifiers

3.4.1. Introduction

The two core-shell rubber modifiers studied both had a functionalised shell of poly(methyl methacrylate) and a diameter of about 100 nm. However, they had different rubbery cores: (a) polybutadiene (CSi) or (b) styrene-butadiene copolymer (CSii). The basic properties of these modifiers are given in Table 3 and they were both used at a concentration of 10 wt.% of the modifier in the unmodified epoxy-polymer.

3.4.2. Microstructural studies

The two core-shell rubber modifiers do not dissolve in the epoxy resin. Thus, the values of the values of T_g of the epoxy-matrix phase in the '10CSi epoxy-polymer' and the '10CSii epoxy-polymer' are not significantly different from that of the unmodified epoxy-polymer, as may be seen from Table 4. The core-shell rubber particles were clearly visible as well-dispersed spherical particles from the AFM studies. This may be seen from Fig. 6 for the '10CSii epoxy-polymer'. Furthermore, for both the '10CSi epoxy-polymer' and the '10CSii epoxy-polymer' the agreement between the theoretical volume fractions of added particles that should be present and the value determined experimentally from the AFM studies was very good.

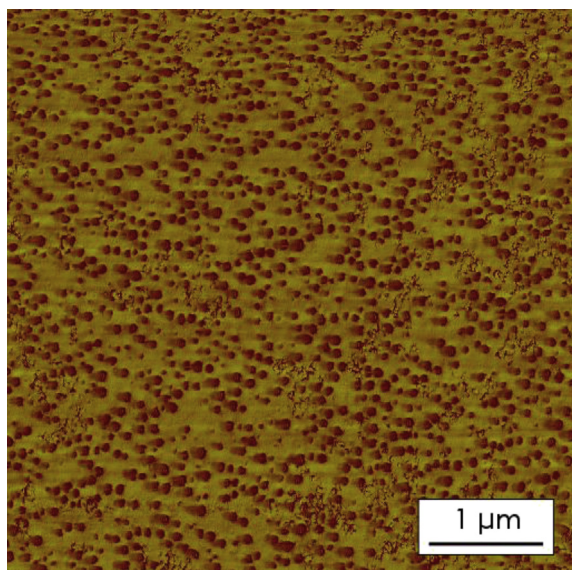


Fig. 6. AFM micrograph of the '10CSii epoxy-polymer'.

3.4.3. Mechanical properties

From Table 4, it may be seen that, as expected, the values of the modulus, E , and the tensile yield stress, σ_{yt} , for the two core-shell rubber modified epoxy-polymers are significantly lower than that of the unmodified epoxy-polymer. However, the value of the compressive strain at failure, ϵ_{fc} , is not significantly different for the '10CSi epoxy-polymer' but is somewhat higher for the '10CSii epoxy-polymer', compared to that of the unmodified epoxy-polymer.

The values of the quasi-static fracture energy, G_{IC} , for the two core-shell modified materials are dramatically greater than for the unmodified epoxy-polymer. Indeed, for the '10CSii epoxy-polymer' the value of G_{IC} is 2540 J/m², which is a factor of about five greater than the value of G_{IC} for the unmodified epoxy-polymer. On the other hand, the value of G_{th} from the cyclic-fatigue tests is not very different for either the '10CSi epoxy-polymer' or the '10CSii epoxy-polymer', compared to the unmodified epoxy-polymer, see Table 4.

From the plot of the cyclic-fatigue threshold fracture energy, G_{th} , versus the fracture energy, G_{IC} , for these various polymers, see Fig. 2, then the increases seen in the values of G_{IC} , are very evident. Unfortunately, the presence of the core-shell rubbers in the epoxy-blend polymers gives no major increase in the cyclic-fatigue resistance, as measured via the values of G_{th} .

3.4.4. Toughening mechanisms

For the '10CSi epoxy-polymer', the SEM micrographs, see Fig. 7, of the fracture surfaces clearly show that the core-shell rubber particles have cavitated. Further, they reveal that plastic void growth of the epoxy-matrix phase has occurred, as the observed voids are larger in diameter than the rubber cores of the particles seen in the AFM images. This toughening mechanism leads to a significant increase in the measured fracture energy, G_{IC} , to 1940 J/m². However, this is not the tougher of the core-shell epoxy-blend formulations, since the strain to failure of the '10CSi epoxy-polymer' is essentially unchanged from the value for the unmodified epoxy-polymer, and hence the extent of plastic void growth that can occur is relatively small. Under cyclic-fatigue loading, virtually no cavitation of the core-shell particles was observed for this epoxy blend, as may be seen from comparing Figs. 7 and 8. Hence, no increase in the value of G_{th} was recorded.

For the '10CSii epoxy-polymer', cavitated rubber particles can be readily seen on the fracture surfaces from the quasi-static fracture tests, see Fig. 9. For this modified epoxy-polymer, the fact that it possesses a somewhat higher strain to failure, compared to the 'CSi

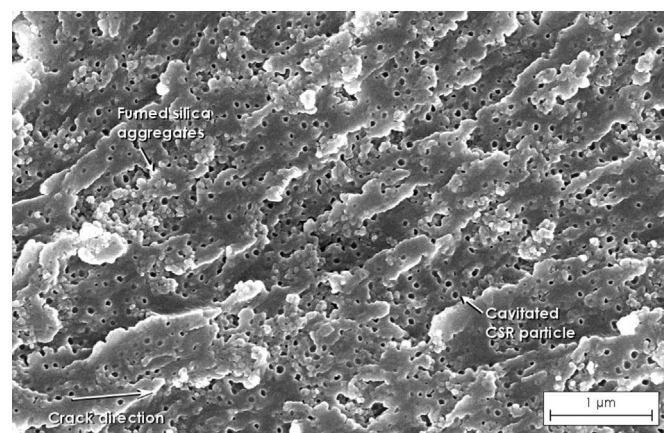


Fig. 7. SEM micrograph of the quasi-static fracture surface of the '10CSi epoxy-polymer'. (The fumed silica aggregates and the cavitated core-shell rubber (CSR) particles are indicated on the figure.)

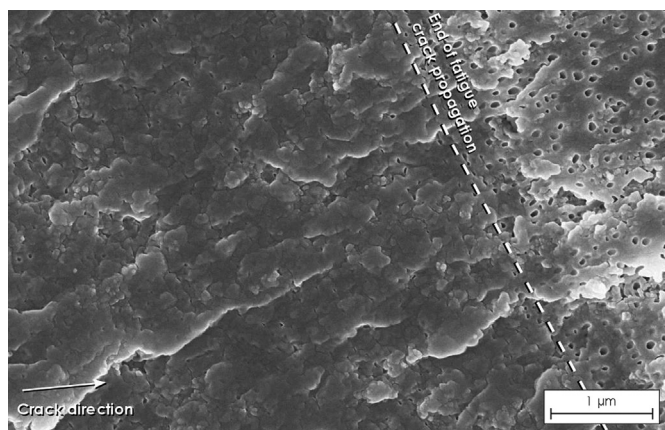


Fig. 8. SEM micrograph of the cyclic-fatigue fracture surface, at the threshold, G_{th} , value, of the '10CSi epoxy-polymer'.

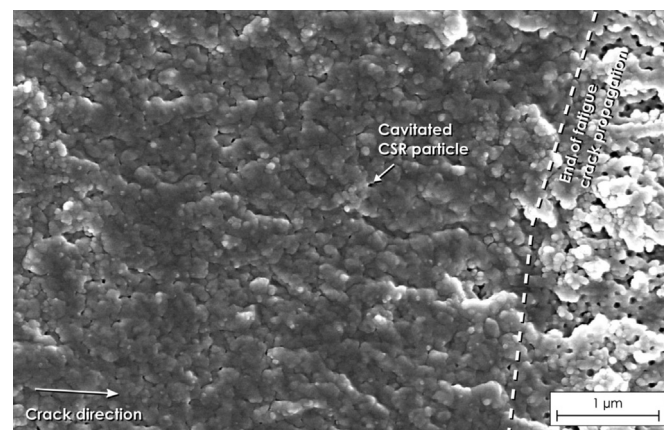


Fig. 10. SEM micrograph of the cyclic-fatigue fracture surface, at the threshold, G_{th} , value, of the '10CSii epoxy-polymer'. (The cavitated core-shell rubber (CSR) particles are indicated on the figure.)

epoxy-polymer', see Table 4, leads to more extensive plastic void growth and hence a higher value of the fracture energy, G_{Ic} . Under cyclic-fatigue loading, there was a small degree of cavitation of some of the core-shell particles, see Fig. 10. Hence, the increase in the threshold fracture energy is correspondingly small, with a value of G_{th} of 195 J/m² being measured compared to 155 J/m² for the unmodified epoxy-polymer.

3.5. 'Hybrid' modifiers

3.5.1. Introduction

The very dramatic effect that the presence of the core-shell rubbers in the epoxy-blend formulation had upon the value of the quasi-static fracture energy, G_{Ic} , but the very little effect such modifiers had upon the cyclic-fatigue value of G_{th} , led to the idea of combining the two different types of modifiers studied in the present work. That is, to combine the core-shell rubber particles with a simple polymeric-modifier to give 'hybrid' modified epoxy-polymers. The various 'hybrid' modified epoxy-polymers that were studied are listed in Table 4.

3.5.2. Microstructural studies

Since the core-shell rubber modifiers (i.e. CSi and CSii) are not soluble in the epoxy resin, the values of T_g of the epoxy-matrix

phase of the 'hybrid' modified epoxy-polymers are essentially governed by the type and concentration of the simple polymeric-modifier that is present, as is illustrated by the values shown in Table 4.

Considering the microstructures, then the 'hybrid' modified epoxy-polymers exhibited the microstructures as expected from the studies reported above. In the case of the '10PS + 10CSii hybrid epoxy-polymer' the PS modifier was always fully soluble in the epoxy-matrix phase and the core-shell rubber particles were clearly visible as well-dispersed spherical particles. For the '10PPGm + 10CSi', '10PPGm + 10CSii' and '10PU + 10CSii hybrid epoxy-polymers', the form of the phase of the simple polymeric-modifier was very similar to that observed when each modifier was present by itself, see above. However, the core-shell rubber particles were not as well dispersed in these 'hybrid' epoxy-polymer blends, compared to the formulations using only the core-shell rubber particles, but exhibited a slight tendency to aggregate to form 2 μm sized agglomerates.

3.5.3. Mechanical properties

The values of the mechanical properties are given in Table 4. The values of the modulus, E , and the tensile yield stress, σ_{yt} , for the various 'hybrid' formulations are essentially as expected from the previous discussions. However, the values of the compressive strain at failure, ϵ_{fc} , are notably far greater for the '10PU + 10CSii hybrid epoxy-polymer' compared to that for the unmodified epoxy-polymer and for when the PU and CSii modifiers were used individually. Indeed, for this 'hybrid' epoxy-blend a value of ϵ_{fc} of 122% was recorded, albeit with a significant decrease of the yield stress, σ_{yt} .

Now, as may be seen from Table 4, the three 'hybrid' formulations with the highest values of ϵ_{fc} do indeed exhibit relatively high values of G_{Ic} . These same three 'hybrid' formulations also exhibit relatively high values of the cyclic-fatigue threshold, G_{th} , value. Although it is noteworthy that the '10PU + 10CSii hybrid epoxy-polymer' has the highest value of G_{th} .

The above comments are readily seen from Fig. 2, where the very good fracture performance, with respect to relatively high values of both G_{Ic} and G_{th} , are especially evident for the '10PPGm + 10CSi' and the '10PU + 10CSii hybrid epoxy-polymers'.

3.5.4. Toughening mechanisms

For the '10PS + 10CSii hybrid epoxy-polymer', cavitated rubber particles can be readily seen on the fracture surfaces, see Fig. 11.

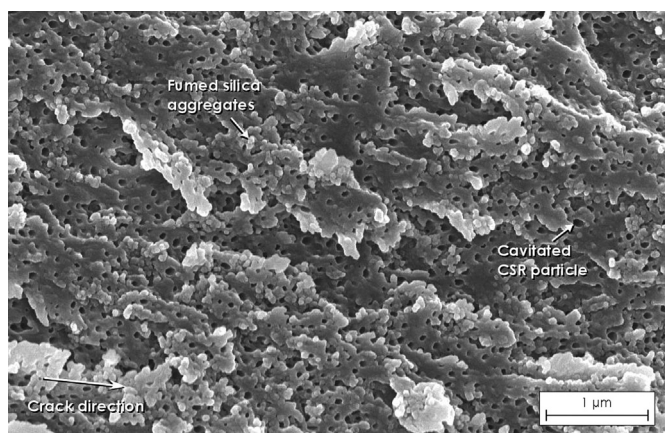


Fig. 9. SEM micrograph of the quasi-static fracture surface of the '10CSii epoxy-polymer'. (The fumed silica aggregates and the cavitated core-shell rubber (CSR) particles are indicated on the figure.)

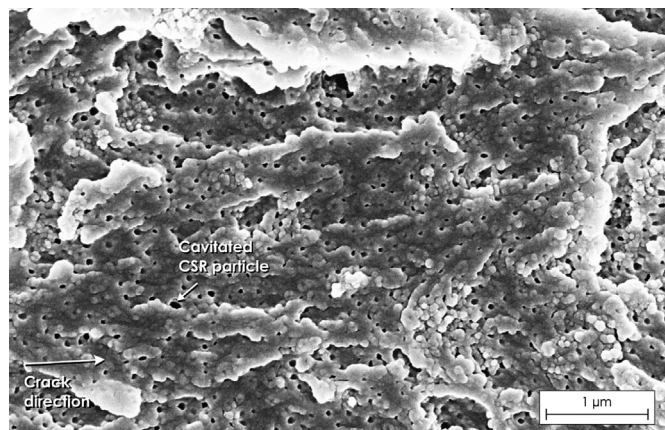


Fig. 11. SEM micrograph of the quasi-static fracture surface of the '10PS + 10CSii hybrid epoxy-polymer'. (The cavitated core-shell rubber (CSR) particles are indicated on the figure.)

However, the extent of the plastic void growth is relatively small in diameter, which reflects the relatively low value of ε_{fc} that was measured for this epoxy-polymer blend, see Table 4. This suggests that less energy is absorbed by plastic void growth of the epoxy-matrix phase than for some of the other formulations. Thus, the toughening effect is significant, but not as large as for the other 'hybrid' systems studied. After the cyclic-fatigue tests, analysis of the fracture surfaces showed that only a very few of the core-shell rubber particles had cavitated, and indeed there was no significant effect on the measured threshold fracture energy, G_{th} .

The fracture surfaces of the '10PPGm + 10CSi', '10PPGm + 10CSii' and the '10PU + 10CSii hybrid epoxy-polymers' all showed cavitated rubber particles. In all cases the yield stress is reduced and the strain to failure is increased for these epoxy-polymer blends, compared to the unmodified epoxy-polymer, see Table 4. The values of the fracture energies of the '10PPGm + 10CSi' and the '10PU + 10CSii hybrid epoxy-polymers' are relatively very high and not significantly different. This indicates that, given the necessary multiphase microstructure, it is possible to achieve a good toughness with (i) a reasonably high yield stress and a moderately high strain to failure, or alternatively (ii) with a relatively low yield stress and a very high strain to failure for the epoxy-matrix phase. However, for the '10PPGm + 10CSii' material, the value of the fracture energy is lower since, although the yield stress is low, the strain to failure is not that high. Hence, the toughness of the '10PPGm + 10CSii hybrid epoxy-polymer' is lower than that of either the '10PPGm + 10CSi' or the '10PU + 10CSii' materials. Comparing the '10PPGm + 10CSi' and the '10PPGm + 10CSii' epoxy-polymer blends reveals that the type of CSR particles which gave the better performance when they were employed as a single modifier do not necessarily give a higher toughness when used in a 'hybrid' epoxy-polymer blend. This observation appears to arise due to the values of σ_{yt} and ε_{fc} of the epoxy-matrix phase being different for the two types of added CSR particles, and the influence that these properties have on the degree of plastic deformation which is involved in the toughening mechanism; and is reflected in the value of G_{lc} .

Under cyclic-fatigue loading, for the '10PPGm + 10CSi hybrid epoxy-polymer', the core-shell rubber particles cavitated and the measured value of G_{th} was 330 J/m². The '10PPGm + 10CSii hybrid epoxy-polymer' exhibited a similar toughening mechanism, and the value of G_{th} was not significantly different, being 300 J/m². Analysis of the fracture surface of the '10PU + 10CSii hybrid epoxy-polymer' also showed cavitated rubber particles and subsequent

plastic void growth, but the higher value of the strain to failure led to a somewhat higher value of G_{th} of 440 J/m².

Finally, it should be noted that the toughening performance of the '10PU + 10CSii hybrid epoxy-polymer' is not significantly different from that of the '10PU epoxy-polymer', both under quasi-static and cyclic-fatigue loading. This again emphasises that for multiphase polymer-blends the properties of the epoxy-matrix phase plays an important role. Given that the appropriate multiphase microstructure is attained, it is possible to achieve a good toughness with either (i) a reasonably high yield stress and a reasonably high strain to failure (i.e. as in the '10PU epoxy-polymer'), or (ii) with a low yield stress and a very high strain to failure (i.e. as in the '10PU + 10CSii hybrid epoxy-polymer').

3.6. Optimised hybrid-modifiers

3.6.1. Introduction

From studying the mechanisms of toughening, a multiphase microstructure has been found to be critical in leading to relatively high values of G_{lc} and G_{th} , as the second-phase particles initiated increased plastic deformation in the epoxy-matrix phase via localised shear-banding and/or via debonding/internal cavitation followed by plastic void growth. This increased plastic deformation in the epoxy-matrix phase was the major source of energy dissipation. Further, the extent of the energy dissipated is also clearly greatly influenced by the ductility exhibited by the epoxy-matrix phase. Thus, the toughness is affected by the yield stress and plastic failure strain of the epoxy-matrix phase. To test these observations an additional 'hybrid' was formulated by increasing the percentage of the modifiers employed.

Now, from the above results, the '10PS + 10CSii hybrid epoxy-polymer' formulation showed localised shear-yielding and cavitation of the core-shell rubber particles followed by plastic deformation of the epoxy-matrix phase matrix. The addition of the PS modifier to the 'hybrid' polymer-blend gave a relatively low yield stress and high plastic strain, but the increase in G_{lc} was lower than that observed for some of the other 'hybrid' epoxy-polymer blends. These results suggested that a higher percentage of the PS modifier may be beneficial, as might a somewhat higher concentration of core-shell rubber particles. Thus, a '20PS + 15CSii hybrid modified epoxy-polymer' was formulated for further study.

3.6.2. Microstructural studies

The '20PS + 15CSii hybrid epoxy-polymer' exhibited the microstructure as expected from the studies reported above. The core-shell rubber (CSii) particles were well-dispersed, and the polysulfide remained fully dissolved in the epoxy matrix, lowering the T_g to 77 °C.

3.6.3. Mechanical properties

The values of the mechanical properties are given in Table 4. The modulus, E , and the tensile yield stress, σ_{yt} , are essentially as expected from the above discussions and, indeed, the value of the compressive strain at failure, ε_{fc} , of 143% is notably very high for this '20PS + 15CSii hybrid epoxy-polymer'.

3.6.4. Toughening mechanisms

Scanning electron microscopy of the quasi-static fracture surfaces showed that, for the '20PS + 15CSii hybrid epoxy-polymer', the voids that formed after the rubber particles cavitated are indeed relatively very large, with a mean diameter of 86 nm being measured from the fracture surfaces, see Fig. 12. This is due to the relatively very high value of the strain to failure, ε_{fc} , for the epoxy-matrix phase in this 'hybrid' polymer-blend, see Table 4. The epoxy-polymer blend also showed strain-softening from the measured

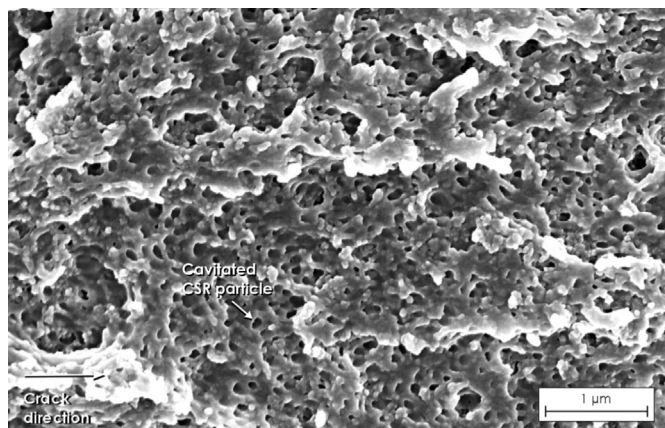


Fig. 12. SEM micrograph of the quasi-static fracture surface of the '20PS + 15CSii hybrid epoxy-polymer'. (The cavitated core-shell rubber (CSR) particles are indicated on the figure.)

compressive stress versus strain curve and hence gave rise to localised shear-banding, as expected. Indeed, the measured fracture energy was the highest of any formulation studied, at 2970 J/m², see Table 4. Under cyclic-fatigue loading, some of the core-shell rubber particles cavitated and the measured value of G_{th} was 300 J/m², which is approximately double the value for the unmodified epoxy-polymer. These values are plotted in Fig. 2, which shows that the '20PS + 15CSii hybrid epoxy-polymer' does indeed show excellent performance in both quasi-static and fatigue fracture, although its value of G_{Ic} is more outstanding than its value of G_{th} .

4. Conclusions

The present work has investigated a range of rubber and thermoplastic materials when used to modify a relatively brittle epoxy polymer to form epoxy-polymer blends with the aim of achieving both a relatively high toughness and a significantly improved cyclic-fatigue behaviour. From studying the mechanisms of toughening that were induced by the addition of the modifier, the presence of a multiphase microstructure in the epoxy-blend modified-polymer was found to be a critical requirement in leading to relatively high values of the fracture energy, G_{Ic} , and of the threshold value of the maximum strain-energy release rate in a fatigue cycle, G_{th} , (below which no significant crack growth occurs). This was due to the second-phase particles initiating plastic deformation in the epoxy-matrix phase matrix, which was the major source of energy dissipation and hence toughening. Nevertheless, the extent of energy dissipated by the plastic deformation of the epoxy-matrix phase was also clearly influenced by the degree of ductility exhibited by the epoxy-matrix phase. Thus, another important feature of the toughening mechanism was the effect that the modifier had upon the yield stress and plastic failure strain of the epoxy-matrix phase by, for example, the modifier being soluble, at least to some extent, in the epoxy-matrix phase.

The unmodified, i.e. 'control', epoxy-polymer examined in the present work possessed a value of G_{Ic} of 495 J/m² and a value of G_{th} of 155 J/m². The addition of a core-shell rubber-particle (CSii) modifier at 10wt.%, based upon a styrene-butadiene rubber core, was found to significantly increase the value of G_{Ic} to 2540 J/m².

However, the addition of this modifier did little to increase significantly the cyclic-fatigue resistance of the epoxy polymer. However, when a 'hybrid' toughening system was formulated which incorporated a core-shell rubber-particle together with a simple polymeric-modifier, that increased the ductility of the epoxy-matrix phase, then the values of both G_{Ic} and G_{th} could be greatly increased. The best combination of such properties was for a 'hybrid' epoxy-polymer modified with both core-shell rubber-particles (CSii) and a poly(propylene-glycol)-based polyurethane (PU) modifier. The values of G_{Ic} and G_{th} were found to increase to 2570 J/m² and 440 J/m², respectively, for this 'hybrid' epoxy-polymer blend.

Acknowledgements

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