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The toughening of cyanate-ester polymers

Part II *Chemical modification*

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A fracture mechanics approach has been used to investigate how the addition of high-temperature resistant thermoplastic modifiers can increase the fracture energy, G_c, of brittle cyanate-ester polymers. Tests were performed using adhesive joint specimens at −55, 21 and 150°C. The fracture energies of poly(ether sulfone)- and polyester-modified cyanate-ester polymers have been measured and scanning electron microscopy has been used to identify the toughening mechanisms involved. Firstly, it is shown that the addition of 25% by weight of a functionalised poly(ether sulfone) (PES) can increase the fracture energy of the cyanate-ester polymers by more than 800%, with the development of a particulate morphology within the modified polymer. Secondly, it is demonstrated that the use of 20% by weight of a polyester-copolymer elastomer can lead to an increase in the fracture energy of up to ten times that of the unmodified cyanate-ester polymer value. Thirdly, it is shown that several of the chemically-modified polymers developed and tested in the present work have fracture energies which are greater than a typical commercially-available cyanate-ester film adhesive. Finally, the effects of long-term ageing in air at 150°C, for up to 7500 hours, on the properties of unmodified, physically- and chemically-modified cyanate-ester polymers are investigated. It is shown that the measured fracture energies of some of these modified cyanate-ester polymers show no significant effect of such long-term ageing.

1. Introduction

The use of adhesive bonding in industry has increased steadily in recent years, and adhesives have replaced welding and mechanical fasteners in many applications. However, the use of adhesives at high temperatures is limited by their relatively low maximum service-temperatures. Most conventional structural adhesives are rubber-toughened epoxy polymers. However, epoxies are unstable and will degrade when exposed to high temperatures [1] and their maximum service temperature will typically be about 175°C [2]. The maximum service-temperature is also restricted by the presence of the rubber particles [3]. In order for the maximum service-temperature to be significantly increased, a high-temperature resistant resin, such as a cyanate ester, may be used to replace the epoxy resin. However, the second-phase rubber particles also need to be replaced by another material with greater elevated-temperature stability [4, 5]. This replacement material must, of course, also impart a significantly improved toughness to the base resin that is employed, especially since all the temperature-resistant polymers tend to be very brittle. The typical adhesive performance required for these high-temperature applications is the ability to survive for 20,000 hours in air at 150°C, with a glass transition temperature, T_g, above 250°C.

The alternatives to epoxy-based polymer systems include cyanate-ester polymers. Cyanate-ester polymers are known to possess good long-term thermal stability [6] and their glass transition temperatures can be very high, typically around 290°C [7, 8]. Cyanate ester monomers are esters of bisphenols and cyanic acid, which contain reactive ring-forming —O—C≡N groups, see Fig. 1, and cure to form thermoset polymers. During curing, they form three-dimensional networks of oxygen-linked triazine (cyanurate) and bisphenyl units [9, 10]. However, the resulting polymers are very brittle, and need to be toughened in order to make them useful engineering polymers. This increase in toughness can be achieved by addition of a second phase [11, 12]. However, this second phase must also possess good thermal stability. In Part I of the present work [13], the use of inorganic and thermoplastic particulates, fibres and woven-mats which act to physically modify the base cyanate-ester resins to give a multiphase nano- or micro-structure for the cured polymer was discussed. The effects of percentage loading of the modifiers and test temperature were investigated, and discussed with reference to the toughening mechanisms which were identified. The present paper, Part II, discusses the use of high-temperature resistant thermoplastics to chemically modify cyanate-ester resins.

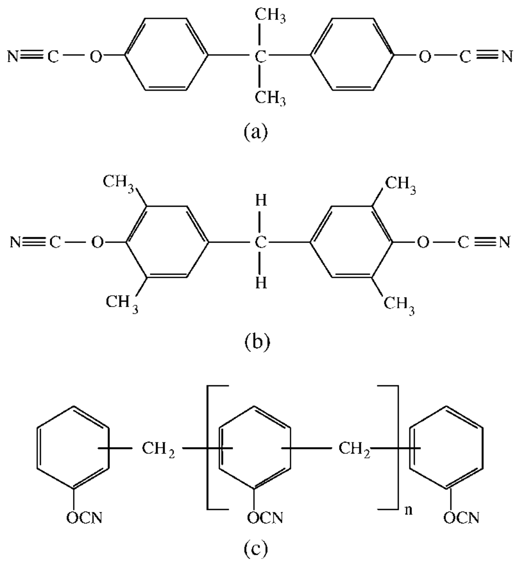


Figure 1 Structural models of the cyanate-ester monomers: (a) bisphenol-A dicyanate (BADCy) monomer, (b) tetramethyl bisphenol-F dicyanate (METHYLCy) monomer, and (c) phenolic triazine (PT) monomer, $n \approx 1.5$ [9].

The blending of two functionally-active thermoplastic modifiers, i.e. a reactively-terminated poly(ether sulfone) and a polyester copolymer, with several different cyanate-ester resins are discussed.

In the present work, the fracture energies, G_c, of unmodified and chemically-modified cyanate-ester polymers have been measured over a range of test temperatures, from −55 to 150°C. These fracture tests have been conducted using the tapered double-cantilever beam (TDCB) adhesive joint geometry, employing surface-pretreated aluminium-alloy substrates. This test method has the advantages that (a) only small quantities of material are needed to conduct a valid fracture-mechanics test, and (b) the surface pretreatment for the substrates can be selected such that cohesive failure through the adhesive layer normally occurs, and this avoids the difficulties that arise in the interpretation of the results when interfacial failure results. The effects on the toughness, G_c, upon the concentration of the added modifiers and the test temperature are investigated. Electron microscopy is used to identify the morphology of the modified polymers and the toughening micromechanisms involved. The relationships between the microstructure of the polymers and the values of the measured toughness are reported. These toughening micromechanisms are also contrasted to those found for the physical modifiers reported in Part I of the present studies. The long-term ageing of adhesive joint specimens (using unmodified, physically-modified and chemically-modified cyanate-ester polymers) in air at 150°C, for up to 7500 hours, is also discussed.

2. Experimental

2.1. Materials

Aluminium-alloy substrates, grade EN-AW-2014A [14], were used for the tapered double-cantilever beam (TDCB) specimens. In part I of the present work [13], only one cyanate-ester monomer was used as a large number of modifiers were investigated. However, in Part II only two modifiers were used, and hence the effect of changing the type of cyanate-ester monomer used could be readily investigated. The cyanate-ester resin monomers used were ‘bisphenol-A dicyanate’ (BADCy), ‘tetramethyl bisphenol-F dicyanate’ (METHYLCy), and ‘phenolic triazine’ (PT) resin, see Fig. 1, supplied by Isola (Düren, Germany). The glass transition temperatures of these polymers are shown in Table I [15].

TABLE I Glass transition temperatures of the unmodified cyanate-ester polymers and of the modifiers

Polymer	Glass transition temperature, T_g (°C) [15]
BADCy	310
METHYLCy	290
PT	325
PES	240
Polyester copolymer	25

Two modifiers were used: (i) a thermoplastic elastomer based on a polyester copolymer (‘Vitel 3200’, Bostik, USA) and (ii) a thermoplastic hydroxyl-terminated poly(ether sulfone) (PES) (‘Sumikaexcel PES5003P’, Sumitomo, Japan) [16]. The glass transition temperatures of these modifiers are 25 and 240°C respectively, see Table I. These modifiers were chosen as the literature indicated that they could provide good toughness and/or high temperature-resistance. Indeed, Porter *et al.* [17, 18] have previously reported that the addition of the polyester-copolymer elastomer gave good short-term high-temperature resistance, as measured by thermogravimetric analysis, plus an increase in the toughness of the BADCy polymer. Kinloch, Yuen and Jenkins [19] showed that the toughness of epoxy polymers could be significantly improved by the incorporation of PES. The toughening effect of PES on a cyanate-ester polymer has also been mentioned by Shimp and Craig [20].

Blends were formulated using between 10 and 30% by weight of the above PES and polyester-modifiers. The monomers were blended with the modifiers and prepolymerised to 44% conversion of cyanate groups [15] by the Institut Fraunhofer Zuverlässigkeit und Microintegration (Teltow, Germany). This was achieved by heating the blend to 180°C and maintaining it at that temperature until the required conversion was reached. The conversion of the cyanate-ester functional groups to s-triazine rings was monitored using Fourier transform infrared spectroscopy (FTIR) via determining the ratio of the —OCN absorbance at 2272 cm^{-1} to the CH_3 stretching peak at 2874 cm^{-1} for the cured resin, and by comparison of this value to that for the monomer. The fractional conversion is given by [1 - (cured resin ratio/monomer ratio)] [21]. In addition, a film adhesive was prepared by the Institut Fraunhofer Zuverlässigkeit und Microintegration using the 20% polyester-modified BADCy resin with a glass scrim [15]. Finally, for comparison, a typical commercial cyanate-ester based film adhesive (‘Metlbond 2555G’, Cytec, USA), was also studied.

2.2. Specimen manufacture

Prior to bonding, the substrates for the TDCB specimens were abraded using 180/220 mesh alumina grit, solvent cleaned in hot trichloroethylene, and etched [22] in chromic-sulphuric acid for 20 minutes at 69°C. The substrates were rinsed with tap water, placed in a bath of tap water for 10 minutes, and rinsed with distilled water. The substrates were then placed in an oven at 140°C for 30 minutes. The prepolymerised resin, which was solid at room temperature, was ground into a powder. The powdered resin was placed on the warm substrates, allowed to melt, and spread over the substrate using a spatula. Wire shims, 0.25 mm in diameter were placed at either end of the substrates to control the thickness of the cyanate-ester adhesive layer. A piece of release-coated aluminium foil was placed on each substrate, extending approximately 80 mm from the loading point, to act as a starter crack. The joints were cured for 16 hours at 180°C, 4 hours at 220°C followed by 1 hour at 260°C, and allowed to cool slowly in the oven.

For the specimens made using the commercial 'Metlbond 2555G' adhesive, the substrates were surface pretreated as described above. The cyanate-ester film adhesive, which was sandwiched between two protective backing films, was cut using a scalpel to be a few millimetres wider than the TDCB substrate. One piece of backing film was removed, and the adhesive applied to one substrate. The other piece of backing film was removed, an aluminium starter foil was placed in position and the second substrate was added. (Wires were not needed to control the bondline thickness in these joints.) The joints were cured for 4 hours at 180°C, followed by 2 hours at 230°C, and then allowed to cool slowly in the oven.

2.3. High-temperature ageing

TDCB specimens were manufactured using (a) the unmodified BADCy, (b) the 10% mica-modified BADCy (mean mica particle size 40 μm) [13], (c) the 20% PES-modified BADCy, and (d) the 20% polyester-modified BADCy materials. The specimens for ageing were placed in an oven at 150°C. One specimen of each type of polymer was removed after 2500, 5000 and 7500 hours.

2.4. Fracture mechanics tests

Fracture testing of the TDCB specimens was performed at a constant displacement rate of 0.1 mm/min, according to the method described in the draft ESIS (European Structural Integrity Society) protocol [23, 24]. Six specimens using each polymer were tested. These fracture tests were performed at −55, 21 and 150°C. Prior to testing, the length of the aluminium starter foil was measured, and any excess adhesive was removed from the side of the specimens. One side of each specimen was spray-painted with a thin layer of white paint, and a paper scale, marked every 1 mm, was adhered to the side of the specimen above the adhesive layer.

The specimens were loaded at a constant displacement rate of 0.1 mm/min until a crack was seen to propagate from the starter foil, when they were unloaded to zero load at 0.5 mm/min. This precracking stage ensures that there is a sharp precrack present in the specimen prior to the actual test. The specimens were loaded again at 0.1 mm/min, and the crack propagation was followed using a travelling microscope. Once about 100 mm of crack propagation had been observed, the specimens were unloaded at 0.5 mm/min. The specimens were then broken open at 5 mm/min. Force, displacement and crack length data were recorded. These data were analysed to provide values of the fracture energy, G_c. Straight lines were fitted to the loading and unloading lines of the force versus displacement response, and the difference in displacement between the displacement axis intercepts was calculated. This offset displacement was divided by the maximum displacement. If the resultant fraction was less than 0.05, then it was assumed that no plastic deformation of the substrates [23]. In the present work, the resultant fraction was always less than 0.05 and, indeed, no plastic deformation of the substrate arms of the TDCB specimens was ever visually observed.

The tapered double-cantilever beam specimen geometry has been used extensively to measure the fracture energy, G_c, of adhesives [25–27]. The TDCB substrates were tapered to give a linear change in compliance, C, with crack length, a. The beams were 310 mm long, 10 mm wide, and the height, z, was defined by a constant, m_b, such that $m_b = 2\ \text{mm}^{-1}$, where m_b is defined by:

$$m_b = \left(\frac{3a^2}{z^3} + \frac{1}{z}\right) \tag{1}$$

The values of the fracture energy, G_c, were calculated using a linear-elastic fracture-mechanics method. The simple beam theory approach was used [23], which yields:

$$G_c = \frac{4P_c^2 m_b}{E_s B^2} \tag{2}$$

where G_c is the adhesive fracture energy, P_c is the failure load, E_s is the substrate modulus, and B is the specimen width.

The crack virtually always grew cohesively through the adhesive layer, by stable or stick/slip propagation. In some cases an 'R-curve' was observed. (An 'R-curve' is where the toughness, i.e. the material's resistance to fracture, increases as the crack grows.) These types of crack growth are explained fully in Part I of the present work [13]. The coefficients of variation for the values of the fracture energy, G_c, so ascertained were typically ±10%, but with ±12% being recorded for the long-term ageing tests as a single specimen was tested for each ageing condition.

3. Results and discussion

3.1. Introduction

The results from the fracture tests will be discussed for each formulation. Firstly, the unmodified BADCy, METHYLCy and PT polymers will be considered. Secondly, the PES- and polyester-modified materials will be discussed. Thirdly, a film adhesive developed from one of the above formulations will be discussed.

Finally, these data will be compared to the results for the commercially-available cyanate-ester system, i.e. the 'Metlbond 2555G' adhesive.

3.2. Unmodified polymers

3.2.1. Unmodified BADCy polymer

The TDCB specimens made with the unmodified BADCy polymer failed by stick/slip crack propagation, and a mean initiation fracture energy of 150 J/m^2 was measured at 21°C. The fracture energy was found to decrease with increasing temperature, see Fig. 2. A scanning electron micrograph of the fracture surface is shown in Fig. 3 and, as with all micrographs in the present paper, the crack propagation is from left to right. This micrograph illustrates features that are typical of the fast fracture associated with stick/slip crack growth in a very brittle material. The fracture surface of the unmodified BADCy polymer is relatively smooth and glassy, showing that little plastic energy dissipation has accompanied the fracture process. However, there are apparent steps and changes of level of the crack. These features are feather markings, caused by the crack forking due to the excess of energy associated with the relatively fast crack growth. The multi-planar nature of the surface and this repeated forking are ways of absorbing this excess energy in a very brittle material during the fast crack propagation phase that follows the crack initiation [28]. A glass transition temperature, T_g, of 310°C was measured for the unmodified BADCy polymer, see Table I.

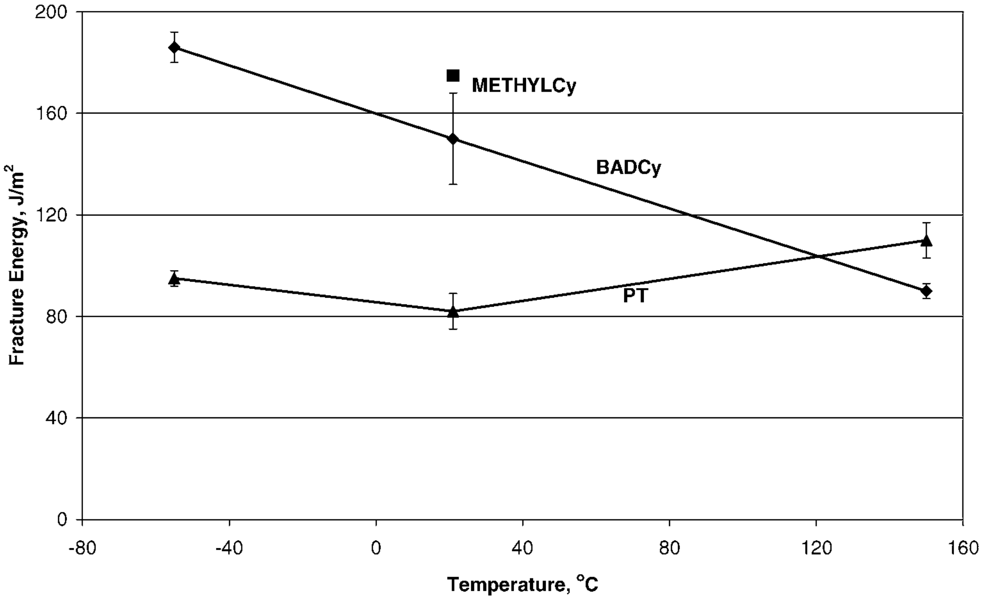


Figure 2 Fracture energies (mean ±1 standard deviation) for the unmodified BADCy, METHYLCy and PT polymers versus test temperature. The data for METHYLCy are taken from the literature [7, 8, 29, 30].

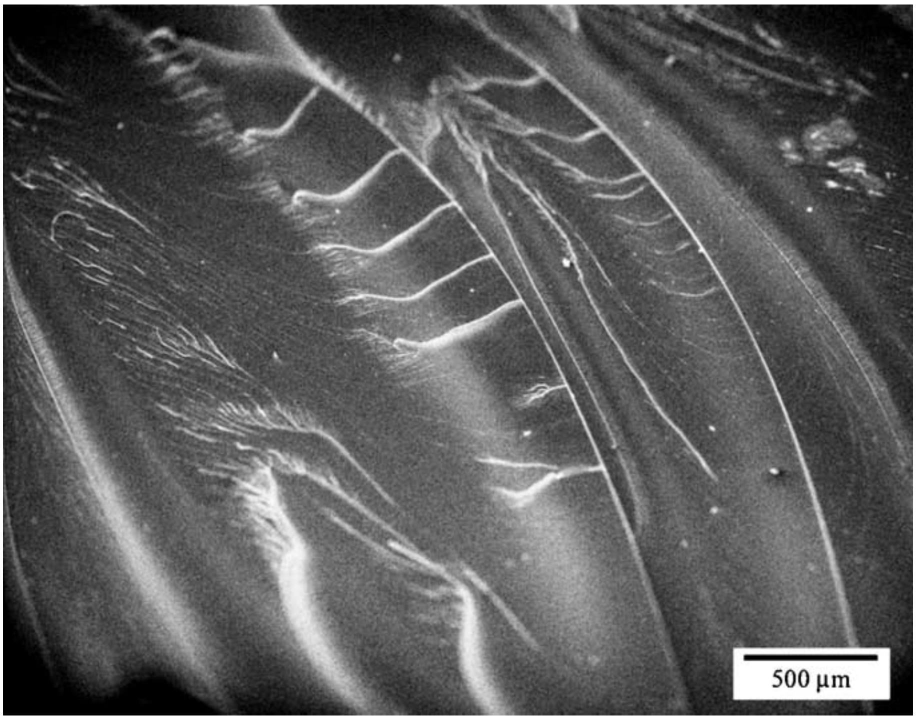


Figure 3 Fracture surface of unmodified BADCy polymer, tested at 21°C.

3.2.2. Unmodified METHYLCy polymer

No tests have been performed on unmodified METHYLCy polymer using the TDCB joint geometry in the present work. A range of fracture energies, from 120 to 175 J/m^2 are quoted in the literature for the unmodified METHYLCy polymer [7, 8, 29, 30]. However, since the value of 175 J/m^2 is the most widely quoted, this value will be used for comparative purposes in the present work. A glass transition temperature, T_g, of 290°C was measured for the unmodified METHYLCy polymer, see Table I.

3.2.3. Unmodified PT polymer

A glass transition temperature, T_g, of 325°C was measured for the unmodified PT polymer. Crack propagation for the PT polymer specimens was in a stick/slip manner at all test temperatures, and a mean initiation fracture energy of 80 J/m^2 was calculated at 21°C. The fracture energy of the PT polymer is approximately constant with increasing temperature, and the PT polymer is the most brittle of the three unmodified polymers studied. Electron microscopy showed that the fracture surfaces were again relatively smooth and glassy, with feather markings caused by the crack forking, as expected for a fast brittle fracture.

3.3. Poly(ether sulfone) modification

3.3.1. PES-modified BADCy polymer

The glass transition temperatures for the PES-modified BADCy polymers are shown in Table II. In all cases the presence of two distinct major peaks from the DMTA experiments indicated that phase separation had occurred to give cyanate-rich and PES-rich phases. The modification of BADCy using up to 20% PES does not reduce the glass transition temperature of the cyanate-rich phase of the modified polymer, and indeed there may even be a small increase in T_g to 315°C. Even for the 25% PES-modified BADCy, the T_g of the cyanate-rich phase of the modified polymer is only 10°C less than that of the unmodified polymer. The PES-modified BADCy polymers were found to have increased fracture energies, as shown in Fig. 4.

TABLE II Fracture energies at 21°C and glass transition temperatures for the PES-modified BADCy polymers

Polymer	Fracture energy, G_c (J/m^2)	Glass transition temperature, T_g (°C) [15] Cyanate-rich phase	PES-rich phase
BADCy	150	310	n/a
10% PES-BADCy	190	315	245
15% PES-BADCy	n/d	315	245
20% PES-BADCy	380	315	250
25% PES-BADCy	330	300	235
30% PES-BADCy	340	n/d	n/d

n/d: not measured.
T_g of PES = 240°C (see Table I).

At 21°C, the 10% PES-modified BADCy polymer gave a fracture energy of 190 J/m^2, a small increase in the value of G_c from 150 J/m^2 for the unmodified polymer. Hence the toughening effect seen for the 10% PES-modified BADCy polymer is relatively small. Dynamic mechanical thermal analysis (DMTA) indicated that the polymer has a two-phase structure, and that the glass transition temperatures of the cyanate-rich and PES-rich phases are very similar to those of the corresponding unmodified polymers, indicating that no significant amount of PES has dissolved into the cyanate, see Tables I and II. Recent work using transmission electron microscopy by Chang and Hong [31] on the microstructure of 10% PES-modified BADCy has shown that the PES phase is present as very small particles, which were 0.35 μm in diameter in their case. It has been shown that it is very difficult for particles this small in size to cavitate and hence, the toughening effect would not be significant [32, 33], as is indeed observed in the present work.

The 20% PES-modified BADCy polymer gave approximately equal values of the fracture energy at −55 and 21°C, of approximately 380 J/m^2. However, at

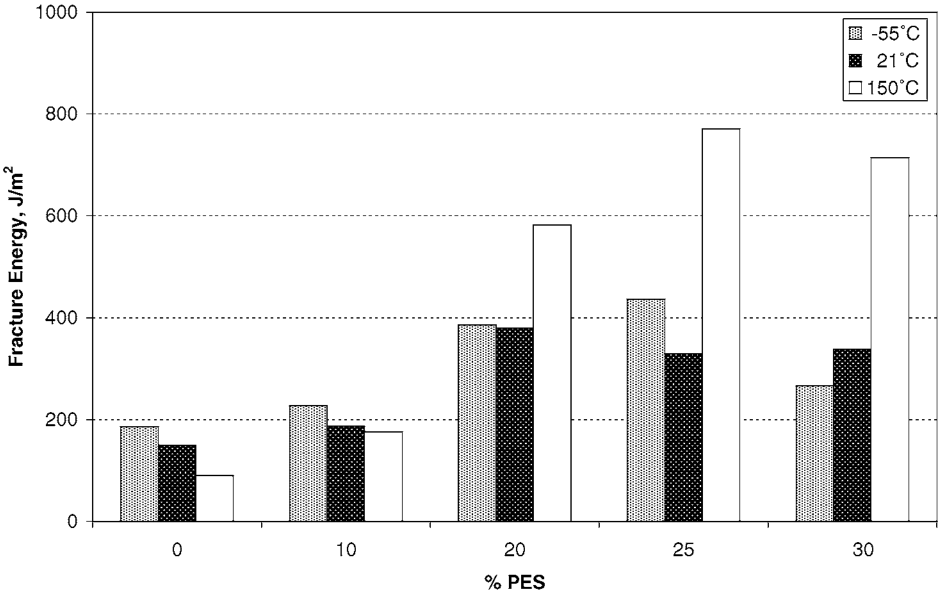


Figure 4 Fracture energies for the PES-modified BADCy polymers versus weight percentage inclusion of PES, tested at −55, 21 and 150°C.

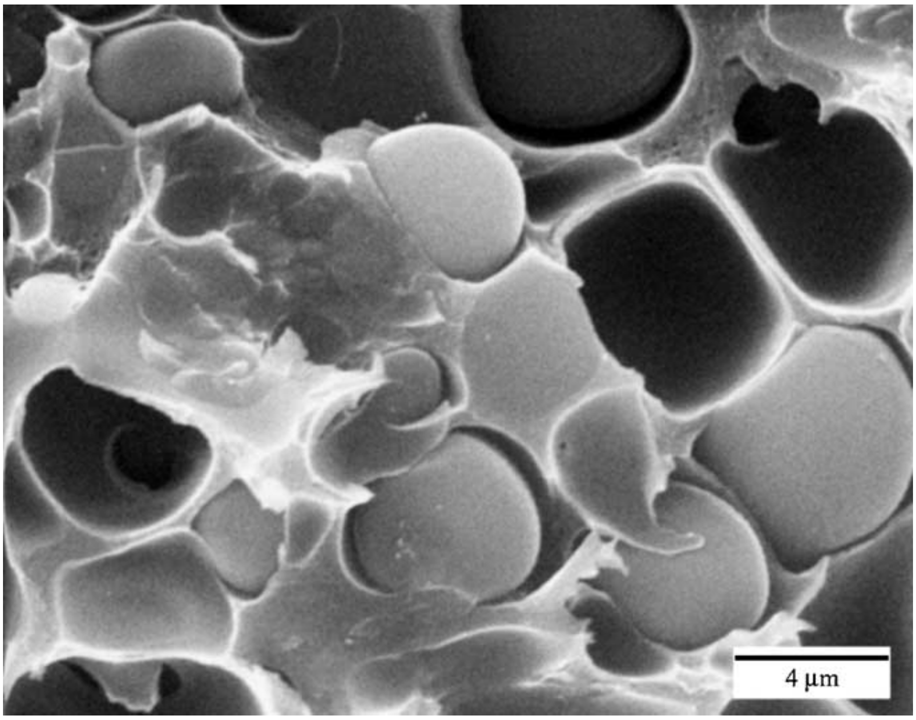


Figure 5 Fracture surface of 20% PES-modified BADCy polymer, tested at 150°C.

150°C, a mean G_c value of 580 J/m^2 was measured, see Fig. 4, compared to 90 J/m^2 for the unmodified BADCy polymer. Scanning electron microscopy of the fracture surfaces showed particles approximately 5 μm in diameter within the continuous phase, see Fig. 5. The DMTA data confirmed the phase-separated structure and indicated that there was little cyanate ester dissolved in the PES, and vice versa.

For the 25 and 30% PES-modified BADCy polymer, fracture energies of approximately 330 J/m^2 were measured at 21°C, compared to 150 J/m^2 for the unmodified BADCy polymer. At 150°C, the fracture energies were increased, as shown in Fig. 4.

For the 20, 25 and 30% PES-modified BADCy polymers, the particles do not appear to be well bonded to the matrix, as the surfaces of the particles are smooth with none of the matrix polymer remaining attached to them. Associated with these particles there is a considerable amount of cavitation, via debonding of the particle and plastic hole growth, as shown in Fig. 5. The micromechanisms of cavitation and plastic hole growth are typically associated with significant energy dissipation [34, 35], and indeed the fracture energy at 150°C is far higher than at −55 and 21°C where these cavities were not observed after fracture testing. In the published literature, Woo *et al.* [36, 37] have observed very similar microstructures using polysulfone-modified cyanate, which they concluded to be phase-inverted morphologies. Hence it is suggested that phase-inversion has occurred in the present work at PES contents of 20% and above, with a continuous PES phase and a particulate cyanate phase.

3.3.2. PES-modified PT polymer

The fracture energy of the unmodified PT polymer was found to be approximately independent of the test temperature over the range −55 to 150°C, the fracture energies lying in the range of 80 to 110 J/m^2. The PES-modification of the PT polymer increased the measured fracture energies, although the fracture energies were approximately constant with both test temperature and inclusion level, see Fig. 6. DMTA showed that a two-phase morphology had been formed, glass transition temperatures of 325 and 240°C being measured for the cyanate- and PES-rich phases respectively. The T_gs of the cyanate-ester and PES phases were virtually unchanged from their original values, indicating that little PES has dissolved into the cyanate ester, and vice versa. Electron microscopy showed that the morphology is composed of particles about 4 μm in diameter which are well bonded to a continuous phase, see Fig. 7. These data indicate that the polymer may show a phase-inverted structure, with particles of cyanate ester within a PES matrix, which fails by ductile tearing of the PES at an approximately constant fracture energy [38, 39]. Indeed, previous work has shown that a phase-inverted structure can form even at these relatively low concentrations of modifier [40–42].

3.4. Polyester modification

3.4.1. Polyester-modified BADCy polymer

The 10% polyester-modified BADCy polymer gave a room temperature fracture energy of 400 J/m^2, compared to 150 J/m^2 for the unmodified polymer. A large effect of test temperature was observed, see Fig. 8. The 20% polyester-modified BADCy polymer gave the greatest fracture energy of the chemically-modified materials, a fracture energy of 1970 J/m^2 being measured at 21°C compared with 150 J/m^2 for the unmodified polymer of, see Fig. 8. At −55°C the value of G_c was only 510 J/m^2, which is relatively poor compared to the room temperature and 150°C values. However, the low-temperature fracture energy was still higher than that of all the other modified cyanate-ester polymers

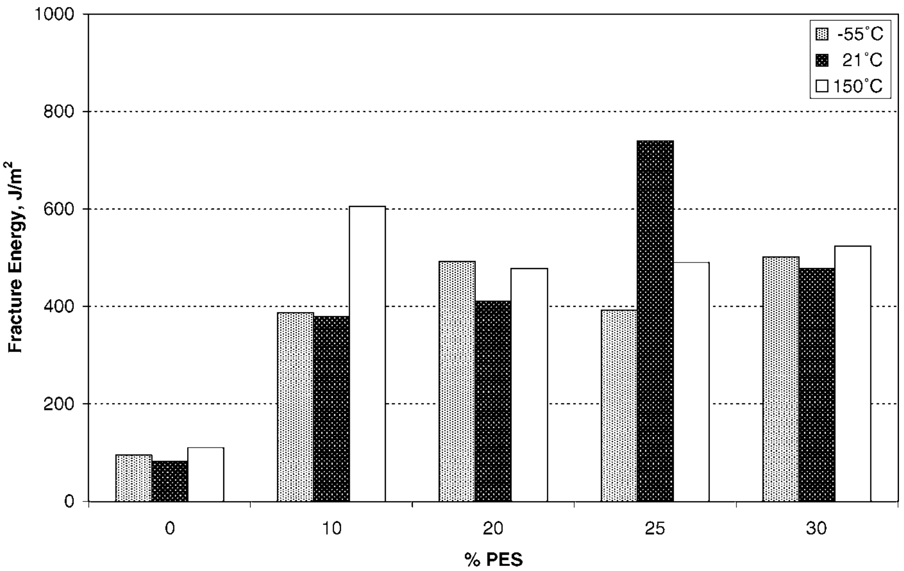


Figure 6 Fracture energies for the PES-modified PT polymers versus weight percentage inclusion of PES, tested at −55, 21 and 150°C.

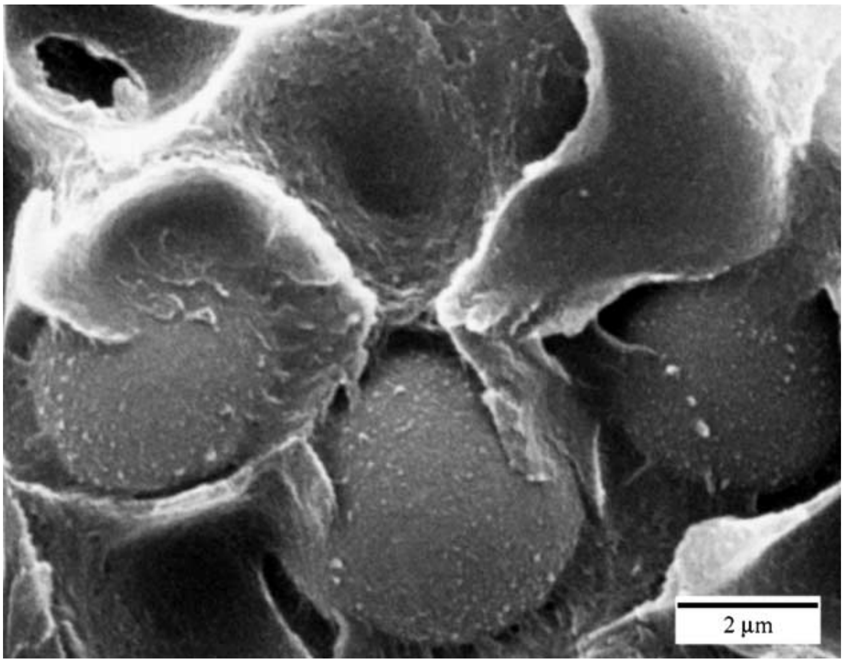


Figure 7 Fracture surface of 10% PES-modified PT polymer, tested at 150°C.

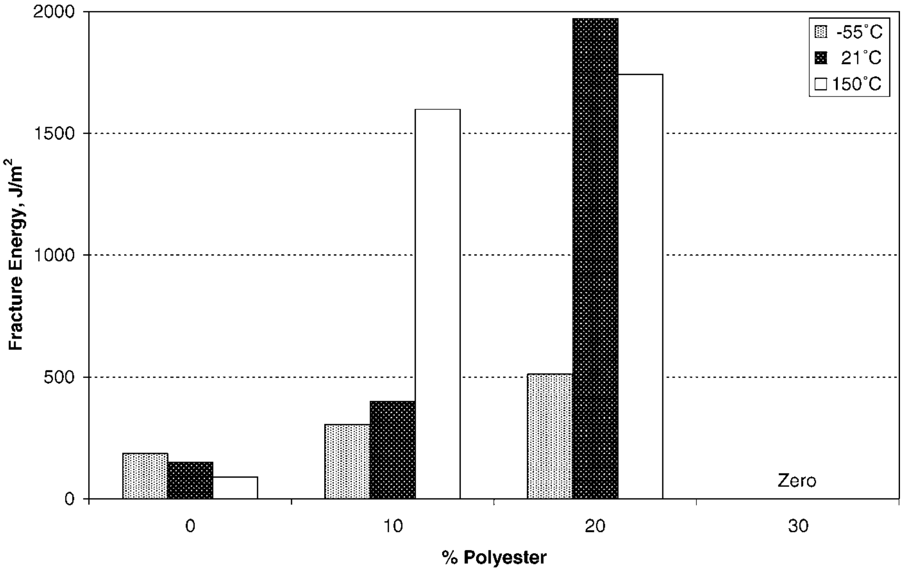


Figure 8 Fracture energies for the polyester-modified BADCy polymers versus weight percentage inclusion of polyester, tested at −55, 21 and 150°C.

TABLE III Fracture energies at 21°C and glass transition temperatures for the polyester-modified BADCy

Polymer	Fracture energy, G_c (J/m^2)	Glass transition temperature, T_g (°C) [15]	
		Cyanate-rich phase	Polyester-rich phase
BADCy	150	310	n/a
10% Polyester-BADCy	400	295	30
15% Polyester-BADCy	n/d	290	25
20% Polyester-BADCy	1970	290	25
30% Polyester-BADCy	0	290	30

n/d: not measured.
T_g of polyester copolymer elastomer = 25°C (see Table I).

examined in the present work. For these polymers, significant blunting was observed at the crack tip during testing, and stress whitening, normally associated with cavitation and hole formation [43], was seen on the fracture surfaces. These toughening micromechanisms absorb energy and lead to the high values of the measured fracture energy.

DMTA indicated that the polyester-modified BADCy had a two-phase structure. The unmodified BADCy polymer had a T_g of 310°C and chemical modification using between 15 and 30% by weight of the polyester elastomer reduced the T_g of the cyanate-rich phase to 290°C, see Table III. Note that the polyester peak was present at 25 to 30°C in all cases. The microstructure of the polyester-modified BADCy polymers, at these relatively low concentrations of modifier, is thought to be composed of elongated particles of the polyester-copolymer elastomeric phase, with a particle size of approximately 1 μm, in the BADCy matrix, although it has been found to be difficult to visualise the microstructure [44].

Attempts were made to produce TDCB specimens using the 30% polyester-modified BADCy polymer, but these joints had no strength when cured, and simply fell apart due to the mass of the aluminium-alloy substrates. The fracture surfaces showed a very large number of air bubbles and failure occurred at the modified-polymer/aluminium-alloy interface, without any polymer being retained on the substrates.

3.4.2. Polyester-modified METHYLCy polymer

DMTA showed that a two-phase morphology was present, see Table IV, with peaks in the tan δ response at 270 and 40°C. The unmodified METHYLCy polymer and polyester copolymer have glass transition temperatures of 290 and 25°C respectively, and hence, the T_g of the cyanate-ester rich phase has been lowered, and that of the polyester-rich phase has been raised, in the modified polymer. These data indicate that a significant amount of polyester has dissolved in the cyanate ester, and vice versa. At 21°C, a mean fracture energy of 357 J/m^2 was measured for the 10% polyester-modified METHYLCy polymer, see Fig. 9. At −55°C, the fracture energy is equal in value to that measured at 21°C, although it is increased to 940 J/m^2, at 150°C.

Increasing the percentage inclusion of the polyester-copolymer elastomer increased the fracture energy of the modified METHYLCy polymer at −55 and 21°C. Scanning electron microscopy of the fracture surfaces

TABLE IV Fracture energies at 21°C and glass transition temperatures for the polyester-modified METHYLCy polymers

Polymer	Fracture energy, G_c (J/m^2)	Glass transition temperature, T_g (°C) [15]	
		Cyanate-rich phase	Polyester-rich phase
METHYLCy	175	290	n/a
10% Polyester-METHYLCy	360	275	40
15% Polyester-METHYLCy	n/d	270	40
20% Polyester-METHYLCy	590	270	40

n/d: not measured.
T_g of polyester copolymer elastomer = 25°C (see Table I).

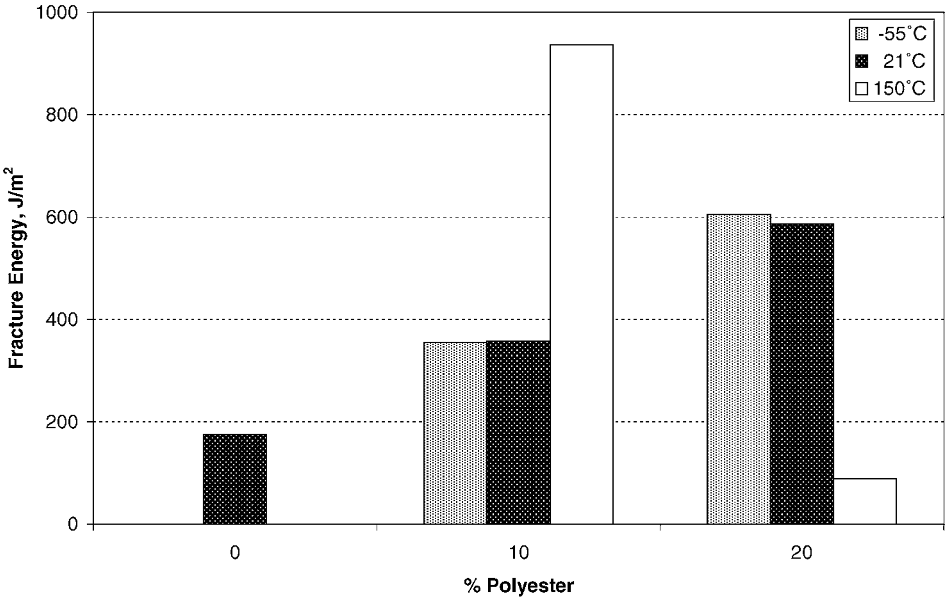


Figure 9 Fracture energies for the polyester-modified METHYLCy polymers versus percentage weight inclusion of polyester, tested at −55, 21 and 150°C. The G_c value for unmodified METHYLCy is taken from the literature [7, 8, 29, 30].

showed a two-phase structure, with particles about 3 μm in diameter within a continuous second phase. The adhesion between the two phases appears to be good. However, at 150°C, the fracture energy was reduced to only 90 J/m^2, due to poor adhesion between the modified polymer and the aluminium-alloy substrates.

3.5. Summary and discussion

3.5.1. *Introduction*

The use of high-temperature resistant thermoplastics to chemically modify the cyanate-ester polymers greatly increased the measured fracture energy of these polymers, and the fracture energy generally increased with the percentage content of modifier. The chemical modification which gave the highest fracture energy was the addition of the polyester-copolymer elastomer to the BADCy polymer, a fracture energy of almost 2000 J/m^2 being measured at 21°C using the 20% polyester-modified BADCy polymer, see Fig. 8. However, a fracture energy of almost 750 J/m^2 could be achieved using the poly(ether sulfone) modifier. Although chemical modification did somewhat decrease the glass transition temperature of the modified polymers, the minimum T_g that was measured for the cyanate ester-rich phase was 270°C: a reduction of only 20°C from the unmodified value. In addition, the DMTA studies indicated that all the modified materials possessed a two-phase morphology. However, the fracture processes and toughening mechanisms differ from one test temperature to another, as expected. Generally, the measured fracture energies of the modified polymers were greater at 150°C than at 21 and −55°C. This was mainly due to the cavitation and plastic hole growth that occurred around the particles during the fracture process at 150°C, and which was not observed at −55 and 21°C. (Exceptions to this observation were found to result when interfacial failure between the modified polymer and the substrates forming the TDCB test specimen occurred at the highest test temperature, so preventing a directly comparable value of G_c being measured.)

3.5.2. *Polyester-modified materials*

The fracture energies of the polyester-modified polymers were much higher than for the unmodified polymer. However, the fracture energies of the polyester-modified METHYLCy polymers were generally lower than those measured for the polyester-modified BADCy, see Figs 8 and 9. DMTA confirmed that a two-phase structure was present in all cases. However, for the BADCy polymer the particles are apparently much smaller than for the METHYLCy [44]. As small particles are difficult to cavitate, the toughening effect is small at −55 and 21°C. However, at 150°C, the test temperature is well above the glass transition temperature of the polyester-rich phase, hence cavitation would more readily occur, and a higher fracture energy would be expected, as was indeed measured. Note that the polyester-modified polymers showed relatively poor interfacial adhesion to the surface-treated aluminium-alloy substrates in some cases, hence some very low values of the fracture energy were measured in these cases.

3.5.3. *PES-modified materials*

3.5.3.1. Based upon the PT cyanate-ester. The fracture energies of the PES-modified PT polymers showed no significant effect of the percentage of PES employed or of the test temperature over the ranges used in the present work, as may be seen in Fig. 6. DMTA showed that all the polymers possessed a two-phase morphology and indicated that little PES has dissolved in the cyanate-rich phase and vice versa. It appears that a phase-inverted morphology has formed, and hence the fracture energy is constant as fracture occurs by tearing of the PES-phase [45].

3.5.3.2. Based upon the BADCy cyanate-ester. The measured fracture energies show a distinct increase between 10 and 20% content of PES in the BADCy polymer, see Fig. 4. For the unmodified and 10% PES-modified BADCy polymers, fracture energies of 200 J/m^2 and below were measured at all temperatures. Thereafter, relatively high fracture energies are measured with increasing PES-content, values of approximately 350 J/m^2 being recorded at −55 and 21°C and of 700 J/m^2 at 150°C. The two main conclusions that may be drawn from these data are that (i) there is a transition between relatively low and higher fracture energies between PES-contents of 10 and 20%, and (ii) at PES-contents of 20% and above the fracture energy at 150°C is much greater than the G_c values measured at −55 and 21°C.

The transition between relatively low and higher fracture energies between PES concentrations of 10 and 20% is due to the change in morphology, i.e. the observed size of the phase separated particles, which occurs between 10 and 20% content of PES in BADCy. This effect of the fracture energy only increasing significantly when there is a marked phase separation was identified by Kinloch *et al.* [19] using PES-modified epoxy polymers. This is combined with a suggested phase-inversion which occurs at PES contents of 20% and above [36, 37], hence the fracture energy at these concentrations is approximately constant.

At −55 and 21°C, fracture of the PES-modified BADCy polymers apparently occurs with no debonding of the particles. However, at 150°C, cavities form between the particles and the matrix, absorbing energy and causing the large increase in the measured fracture energy, see Fig. 4. The adhesion between the particles and the matrix appears to be relatively poor as the debonded particles are very clean and smooth, in contrast to the PES-modified PT polymers, as may be seen by comparing Figs 5 to 7. Note that the propagation of the crack along the PES-BADCy interface has been observed for a hydroxyl-functionalised PES-modified BADCy polymer by Chang and Hong [31], with cavitation and plastic deformation on the matrix side of the interface being observed. Finally, in Part I of the present work [13], debonding and cavitation was observed using the physically-modified polymers which is similar to that observed in the present work, and for both the physically- and chemically-modified cyanate-ester polymers, this plastic hole growth was most evident at 150°C.

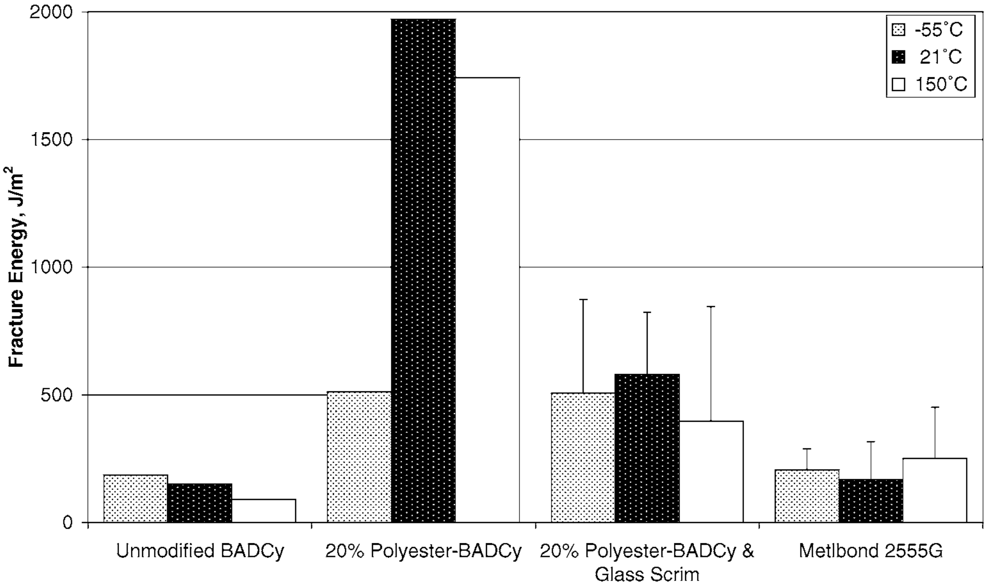


Figure 10 Fracture energy versus temperature for the unmodified BADCy polymer, 20% polyester-modified BADCy polymer, 20% polyester-modified BADCy with glass-scrim film adhesive, and Metlbond 2555G, tested at −55, 21 and 150°C. (The column represents the fracture energy for crack initiation, and the bar represents the maximum value of any *R*-curve observed.)

3.6. Combined chemical and physical modification

3.6.1. Polyester-modified and glass-scrim film adhesive

A film adhesive was produced using the 20% polyester-modified BADCy polymer supported on glass carrier-scrim [15]. This material showed a small '*R*-curve' when tested at room temperature, i.e. the value of the fracture energy, G_c, increased by only a relatively small extent as the crack propagated through the TDCB specimen. The mean initiation fracture energy at 21°C was 580 J/m^2, with a maximum value of 825 J/m^2, and there was little effect of test temperature, see Fig. 10. Visual examination and microscopy of the fracture surfaces of the showed that the fracture occurred at the interface between the modified-polymer and glass carrier-scrim at all test temperatures, see Fig. 11.

It should be noted that a much lower fracture energy was measured for the film adhesive using the 20% polyester-modified BADCy with a glass carrier scrim than was measured for the 20% polyester-modified BADCy polymer alone, see Fig. 10. This was due to a change in the locus of failure, the crack propagation occurring through the polymer for the unsupported polyester-modified polymer, whilst the crack growth for the glass-scrim supported polyester-modified polymer was at the interface between the scrim and the polymer. Hence a lower fracture energy would be expected for the scrim-supported material, as was indeed measured. In addition, as the crack does not arrest during fracture of the scrim-supported material, the extensive crack blunting observed for the unmodified polymer does not occur and hence a lower fracture energy is measured.

3.6.2. Commercial system

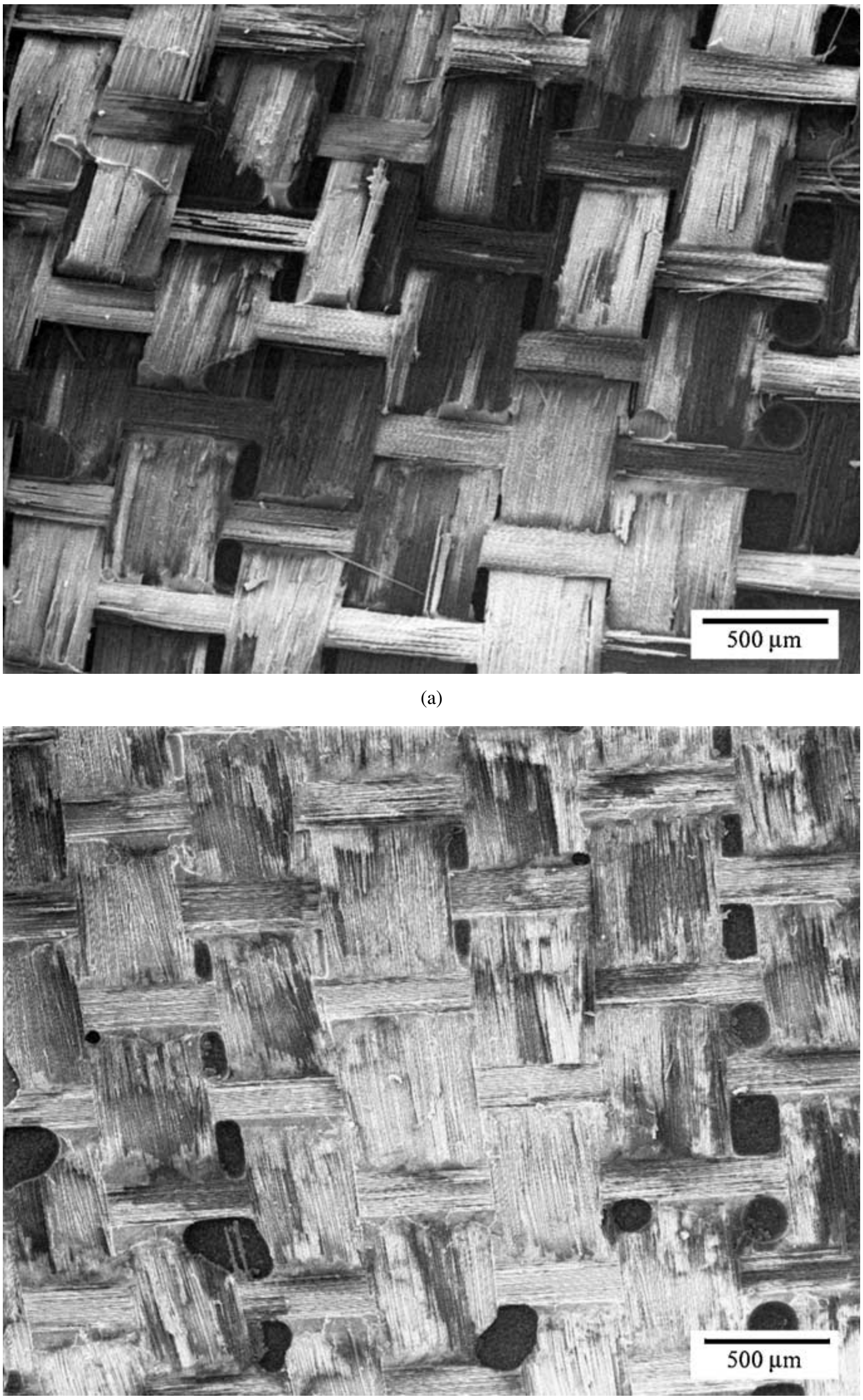
The data from these modifications can also be compared to the fracture energies of the commercial system, Metlbond 2555G, discussed in Part I [13]. The Metlbond 2555G fracture specimens all failed by stable crack propagation with a small *R*-curve being observed. The locus of failure was along the interface between the cyanate-ester polymer and the glass-mat carrier. The glass-mat bridged across the fracture surfaces, leading to increases in the fracture energy as the crack propagates at all the test temperatures, as discussed in Part I [13].

The results for the Metlbond 2555G material are compared in Fig. 10 to the values which were discussed above for the 20% polyester-modified BADCy polymer with a glass scrim. These data show that the modifications in the present work can give significantly greater fracture energies than those measured for the commercially-available adhesive. As may be seen, at all test temperatures the film adhesive produced using the 20% polyester-modified BADCy polymer with a glass scrim has a much higher fracture energy than the commercial system. Fig. 10 also shows that the toughest polymer developed in the present work, the 20% polyester-modified BADCy polymer, is far tougher than the commercial Metlbond 2555G material, room-temperature fracture energies of 1972 and 168 J/m^2 being measured respectively. Further, the glass transition temperature of the Metlbond 2555G is 232°C [2], which is well below that of the unmodified and the chemically-modified polymers used in the present work.

4. High-temperature ageing

4.1. Introduction

Tapered double-cantilever beam (TDCB) specimens were manufactured using unmodified, physically- and chemically-modified polymers. These specimens were aged in air at 150°C, and were removed after 2500, 5000 and 7500 hours. Fracture tests were then performed as described above. The unmodified BADCy polymer was used, together with the BADCy polymer physically-modified with 10% of mica with a mean particle size



(a)

(b)

Figure 11 Fracture surfaces of film adhesive, 20% polyester-modified BADCy polymer with glass scrim, tested at 21°C: (a) mat side, and (b) polymer side.

of 40 μm. The unaged fracture performance of these polymers was discussed in Part I of the present work [13], but is also summarised below. In the case of the chemically-modified cyanate-ester polymers, the 20% PES-modified BADCy and the 20% polyester-modified BADCy polymers were also used for these ageing tests. The glass transition temperatures, measured using DMTA, of the unmodified and the chemically-modified polymers are listed in Table V. In addition, samples of the polymers were scraped off the fracture surfaces after ageing and analysed using differential scanning calorimetry (DSC).

TABLE V Unaged fracture energies at 21°C and glass transition temperatures of the unmodified, physically- and chemically-modified polymers used for the high-temperature ageing

Polymer	Fracture energy, G_c (J/m^2)	Glass transition temperature, T_g (°C) [15] Cyanate-rich phase	Modifier-rich phase
BADCy	150	310	n/a
10% Mica-BADCy	302	310	n/a
20% PES-BADCy	380	315	250
20% Polyester-BADCy	1972	290	25

4.2. Unmodified BADCy polymer

The unaged and aged specimens using the unmodified BADCy polymer failed in a predominately stick/slip manner. The ageing had no significant effect on the measured fracture energy, all the values lying within 1 standard deviation of the unaged fracture energy of 150 J/m^2, see Fig. 12. Scanning electron microscopy showed that the fracture surfaces, see Fig. 3, were relatively smooth and glassy with feather markings due to the crack forking that is characteristic of the fast fracture associated with stick/slip crack growth in a brittle material, as discussed above.

The unaged polymer was straw-coloured, and there was no colour variation across the fracture surfaces. However, after ageing at 150°C, visual examination of the fracture surfaces revealed that the polymer at edges of the specimen had discoloured, changing from a straw colour to light brown. This discoloration extended to a distance of about 1 mm from either edge of the 10 mm wide specimen. Thus, although about 20% of the bonded area showed discoloration due to the ageing, the fracture energy of the cyanate-ester polymer had not been reduced. The extent of this discoloration remained constant at all the ageing times used. Scanning electron microscopy of the fracture surfaces showed that interfacial failure was present in some areas along the edges of the specimen, as shown in Fig. 13. The width of these interfacial patches was less than that of the visually discoloured area, for example after 7500 hours this strip was about 0.5 mm wide. Further microscopy at a

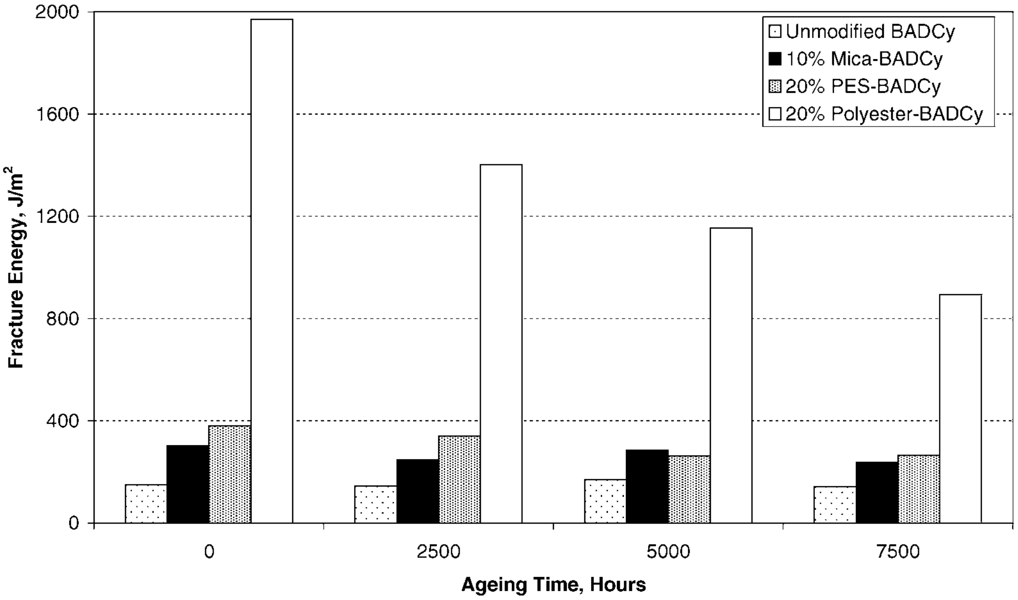


Figure 12 Fracture energies of cyanate-ester based polymers, unaged and aged in air at 150°C. Tested at 21°C.

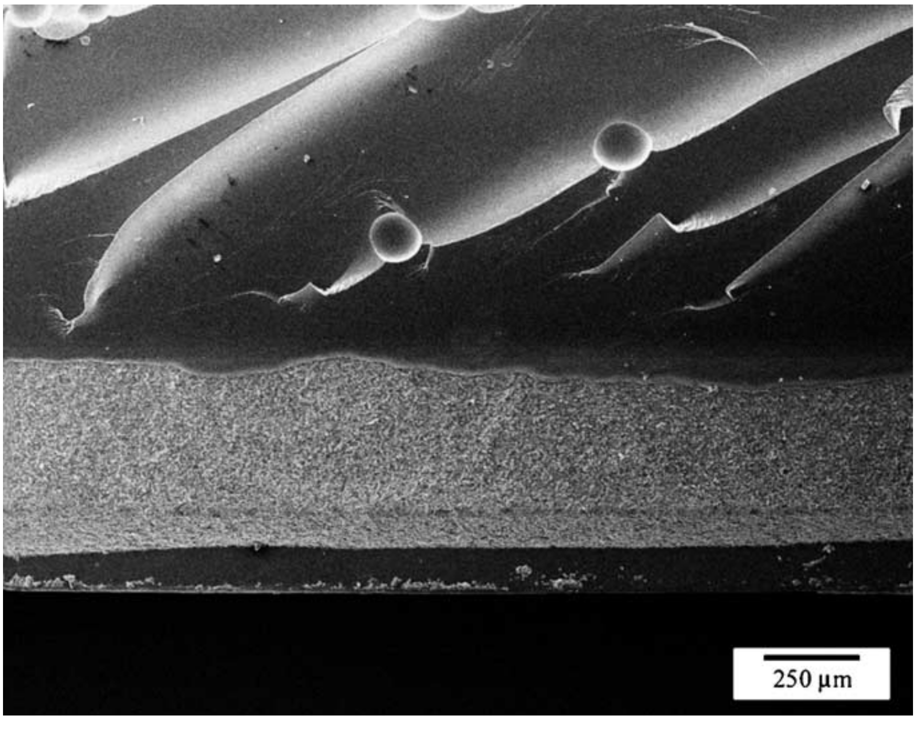


Figure 13 Scanning electron micrograph of fracture surface of TDCB specimen bonded with unmodified BADCy polymer, aged for 7500 hours at 150°C, tested at 21°C.

relatively high magnification confirmed that this was indeed an interfacial failure, with little or no polymer being retained on the aluminium-alloy substrate.

Differential scanning calorimetry showed that the glass transition temperature of the discoloured, oxidised polymer was 50°C lower than that of the polymer from the centre of the specimen. However, the T_g of the straw-coloured polymer was approximately equal to that of the unaged polymer. These data show that the oxidising effect of storage in air at 150°C causes severe degradation of the polymer only at the exposed edges of the specimen.

4.3. Mica-modified BADCy polymer

The unaged specimens made using the BADCy polymer physically-modified with 10% mica (mean particle size 40 μm) failed in a stable manner, with a mean G_c of 302 J/m^2, see Fig. 12. Visually, failure was cohesive within the polymer, with a uniform colour across the fracture surfaces. Scanning electron microscopy of the fracture surfaces showed mica flakes embedded in the polymer and areas where cavitation of the polymer had occurred at the surface of the mica particles were visible [13]. The ageing was found to have no significant effect on the measured fracture energy.

Visual inspection of the aged specimens showed discoloration at the edges of the fracture surfaces, where the polymer changed from its original straw colour to light brown. The extent of this discoloration was constant with ageing time, about 20% of the bonded area being affected. This discoloured polymer had a T_g that was 30°C lower than the polymer in the centre of the specimen, where no discoloration was observed. Hence, there is significant degradation of the polymer at the edges of the specimen, although the change in the measured values of T_g is not as large as was observed for the unmodified BADCy polymer. The presence of the mica platelets may help to protect the polymer, for example by increasing the tortuosity and hence increase the path length need to be taken by oxygen molecules diffusing through the polymer.

4.4. PES-modified BADCy polymer

The unaged 20% PES-modified BADCy specimens failed in a stable manner, and a mean G_c of 380 J/m^2 was measured, as discussed above. Ageing at 150°C reduced the fracture energy significantly, a reduction of 30% being measured after 7500 hours, as shown in Fig. 12.

Discoloration of the edges of the fracture surfaces was visible after ageing, affecting about 20% of the bonded area, and the polymer in these regions was a light brown in colour. There were also strips of interfacial failure at the edges of the aged specimens, although these covered less than 10% of the bonded area. However, apart from these small areas of interfacial failure, the failure was in a cohesive-in-adhesive manner. The glass transition temperatures measured using DSC showed a reduction at the edges of the specimen due to the effect of ageing. The sample of the visually-discoloured polymer at the edges of the specimen gave T_gs for the cyanate-rich and the PES-rich phases that were 20°C lower than the sample from the centre of the fracture surface. Hence the ageing at 150°C has degraded the 20% PES-modified BADCy polymer. Further, both the PES- and the cyanate-rich phases appear to be affected.

4.5. Polyester-modified BADCy polymer

A fracture energy of 1972 J/m^2 was measured for the unaged 20% polyester-modified BADCy polymer. Failure was in a stick/slip manner, and thus the value quoted is an initiation value. During testing, stress whitening was visually observed at the crack tip prior to the crack initiation. Scanning electron microscopy of the fracture surfaces showed them to be relatively featureless, as expected for the fast fracture associated with stick/slip failure.

After 2500 hours of ageing, the mean fracture energy was reduced significantly, see Fig. 12. Further reductions were measured after 5000 and 7500 hours, a mean fracture energy of 894 J/m^2 being measured after 7500 hours at 150°C. This value is approximately half that measured for the unaged specimen. The fracture surfaces showed light brown discoloration at their edges, the affected area increasing with ageing time, from about 18% of the total bonded area after 2500 hours to 30% after 7500 hours. Thus, the reduction in the fracture energy is greater than that which can be attributed to the discoloration even if the discoloured area is assumed to have a fracture energy of zero. However, visual inspection of the fracture surfaces showed that stress whitening, normally associated with cavitation and hole formation [43], was present. This indicates that toughening mechanisms, similar to those observed using the unaged specimens, are occurring during fracture even after ageing at 150°C. However, scanning electron microscopy showed that the edges of the fracture surfaces appeared to have failed in a relatively brittle manner, indicated by the presence of feather markings normally associated with fast brittle fracture. No clear T_gs were visible from the DSC data.

4.6. Discussion

The effect of the ageing of the TDCB specimens at 150°C varied from polymer to polymer. For example, the unmodified BADCy polymer showed no reduction in the measured fracture energy, even after 7500 hours. The BADCy polymer physically modified with mica also showed no significant effect of ageing. However, the fracture energies of the polyester- and PES-modified polymers were significantly reduced; the fracture energy of the polyester-modified BADCy polymer was reduced by over 50% after 7500 hours at 150°C.

Although failure was predominately in a cohesive-in-adhesive manner, interfacial failure was observed at the edges of some specimens after ageing, for example for the unmodified BADCy polymer, as shown in Fig. 13. In the case of the unmodified BADCy polymer, the width of this strip of interfacial failure was observed to increase with ageing time. Hence, there may be a loss of interfacial adhesion during exposure to these high temperatures. However, there is no direct correlation between the area of interfacial failure and the reduction in the measured fracture energy. Indeed, the unmodified BADCy polymer showed no significant reduction in the value of the fracture energy, even when interfacial failure was observed at the edges of the specimen.

The fracture surfaces of the aged specimens exhibited discoloration of the polymers, undoubtedly due to oxidative degradation of the polymer. The glass transition temperature of the discoloured polymer at the edge of the TDCB specimens was reduced compared to the T_g of the straw-coloured polymer in the centre of the fracture surfaces. This reduction, by as much as 50°C for the unmodified BADCy polymer, shows that the polymer has been severely degraded. The colour change indicates that chain scission has occurred, with the formation of more unsaturated groups. The mechanism of thermal degradation of cyanate-ester polymers has not yet been fully established. The short-term stability of cyanate ester polymers is very good, with the onset temperatures for degradation being above 400°C, as measured using thermogravimetric analysis. However, cyanate-ester polymers exposed in air at above 200°C for long times have been observed to fail prematurely by outgassing, i.e. by the evolution of volatile degradation products, although this degradation mechanism was not observed at temperatures below 200°C [29]. Another degradation mechanism, supported by data reported by Hamerton [29] and Lin [46], is that water may react with the unconverted cyanate groups causing carbamate formation, followed by decarboxylation. In addition, hydrolytic cleavage of the ester linkage and subsequent decomposition of the triazine ring may occur. These two mechanisms occur in the presence of water. Although the air in which the TDCB specimens used in the present work were stored should be relatively dry, the polymer will have absorbed some water prior to ageing. The presence of such water would allow these mechanisms to occur. This water will take some time to diffuse from the centre of the joint to the edges, causing a gradual degradation of the polymer. Finally, it should be noted that the presence of the aluminium-alloy substrates might effect the degradation mechanisms. For example, Possart and Valeske [47] postulated that there is carbamate coupling to the aluminium oxide via surface hydroxyl groups. Hence, the loss of interfacial adhesion after ageing noted in the present work may be due to the attack of this linkage at high temperature.

5. Conclusions

A fracture mechanics approach has been used to investigate the effect of the addition of chemical modifiers on the toughness of high-temperature resistant, but brittle, cyanate-ester polymers. Tests were performed using tapered-double cantilever-beam (TDCB) adhesive joint specimens at −55, 21 and 150°C. Three cyanate-ester polymers were used, termed ‘METHYLCy’, ‘BADCy’ and ‘PT’ polymers. Two chemical modifiers were employed: hydroxyl-terminated poly(ether sulfone) (PES) and a polyester-copolymer elastomer. DMTA has been used to measure the glass transition temperatures, T_g, of the unmodified polymers, values of 290, 310 and 325°C being measured for the METHYLCy, BADCy and PT polymers respectively. The fracture energies, G_c, of these unmodified and chemically-modified cyanate-ester polymers have been measured and scanning electron microscopy has been used to determine the toughening micromechanisms involved.

The greatest increase in fracture energy was obtained by the modification using the polyester-copolymer elastomer, a G_c value of 1970 J/m^2 being measured at room temperature using the 20% polyester-modified BADCy polymer compared with 150 J/m^2 for the unmodified polymer. DMTA studies indicated that a two-phase morphology was present in all cases. There was evidence of crack blunting and stress whitening which accompanied the fracture process. Hence, cavitation around the particulate second phase and plastic deformation of the cyanate-ester matrix appear to be the toughening mechanisms operating in these chemically-modified polymers.

For the PES-modified BADCy polymer, a maximum fracture energy of 380 J/m^2 was measured at 21°C. However, at 150°C, the measured fracture energies were much higher than at −55 or 21°C, due to debonding, cavitation and plastic hole growth around the particles. It was also observed that the adhesion between the particles and the matrix was relatively poor compared to the PES-modified PT polymers. The fracture energies of the PES-modified PT polymers were independent of both the amount of PES used and the test temperature due to the formation of an apparently phase-inverted morphology.

The 20% polyester-modified BADCy polymer was used to prepare a film adhesive supported on a glass scrim. The fracture energies were compared to those measured using a commercially-available cyanate ester film adhesive, and were found to be significantly greater at all the test temperatures used. Further, the modified polymers developed in this work also showed higher T_g values than the commercial material.

Finally, various cyanate-ester polymers were aged in air for up to 7500 hours at 150°C. The unmodified and mica-modified BADCy polymers were not significantly affected by ageing. However, the fracture energies of the PES- and polyester-modified polymers were reduced by 30 and 55% respectively after 7500 hours. Electron microscopy of the fracture surfaces showed that failure was predominately cohesive within the polymer, although interfacial failure between the polymer and the aluminium-alloy substrates did occur at the edges of some specimens. The reduction in the measured fracture energy due to ageing was attributed to oxidative damage of the polymers, plus a loss of interfacial adhesion in some cases. The glass transition temperatures of the polymers were reduced by the oxidative damage, the measured T_g at the edge of the specimen being typically 30°C less than that measured in the centre of the specimen, where no oxidative discoloration was observed.

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