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The development of novel functionalised aryl cyanate esters. Part 2. Mechanical properties of the polymers and composites[☆,☆☆]

I. Hamerton[a,*], J.M. Barton[a], A. Chaplin[b], B.J. Howlin[a], S.J. Shaw[b]

[a]*Department of Chemistry, School of Physics and Chemistry, University of Surrey, Guildford, Surrey GU2 7XH, UK*
[b]*Structural Materials Centre, Defence Evaluation and Research Agency, Farnborough, Hampshire GU14 0LX, UK*

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Abstract

Carbon fibre preimpregnated tape (prepreg) was prepared from a range of prepolymers comprising several different blends of alkenyl-functionalised cyanate ester (CE) monomers with commercial CE and bismaleimide (BMI) monomers and blends. Carbon fibre composites were prepared by autoclave moulding. Dynamic mechanical thermal analysis (DMTA) was used to assess cure cycles by the measurement of glass transition temperatures (T_g). Mechanical properties are reported for neat resins and compared with the corresponding composite properties such as interlaminar shear strength, flexural strength, compressive strength and mode I fracture toughness (G_{IC}). By incorporation of alkenyl-functionalised CE monomers into CE/BMI blends it is possible to raise the value of T_g while maintaining levels of G_{IC} (when compared with an unmodified BMI/CE blend) and without leading to a degradation in other mechanical properties. This enhancement in neat resin fracture toughness was translated into the corresponding composite. For example, a novel modifier 5rPOCN, at an incorporation level of 15% by weight, produces a composite with $T_g = 170$°C, interlaminar shear strength 113 MPa and $G_{IC} = 513$ J/m^2, comparable with reported thermoplastic-toughened CE composites. Crown Copyright © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Cyanate esters; Alkenyl groups; Bismaleimides

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1. Introduction

During the last decade, aromatic cyanate ester (CE) resins have emerged as a new class of thermosetting polymers for use as preimpregnated tape (prepreg) matrices in both the aerospace and electronics industries [1]. Since the early 1980s, considerable effort has been expended in the toughening of resin systems and to this end, a variety of methodologies has been employed including: the incorporation of elastomers or engineering grade thermoplastics; the use of specially synthesised thermoplastics, tailored to specific thermoset resins; and the incorporation of particles that act as crack stoppers [2].

While exhibiting superior hot/wet performance to epoxy resins and bismaleimides (BMIs), which are direct competitors for CE resins in aerospace and microelectronics applications, CE resins are somewhat more expensive and are rarely used as homopolymers. Consequently, the blending of CEs with epoxies, BMIs, elastomers and thermoplastics has been examined in a number of studies [3–6] and commercial materials embodying these approaches do exist. For example, Mackenzie and his co-workers [6] have demonstrated that significant levels of fracture toughness (of 340–500 J/m^2) can be achieved in thermoplastic polyethersulphone-modified CE resin composites (compared with 150–170 J/m^2 in the unmodified CE blends and homopolymers). These findings formed the basis for the commercial CE resin system 954-2A. Another family of materials (the Skylex®BT resins) is marketed by Mitsubishi Gas and Chemical Corporation in which 2,2-*bis*(4-cyanatophenyl)isopropylidene (the dicyanate of bisphenol A, DCBA) and *bis*(4-maleimidophenyl)methane (DDM-BMI) are the components of the blend. The proposed chemical path has been reported [4], but the theoretical pyrimidine-type structure arising from this reaction has not been confirmed experimentally [7] and it is now generally accepted that CEs and BMIs do not co-react [8], but instead form an interpenetrating network (IPN). Although such blends are reasonably tough ($G_{IC} = 140$ J/m^2 for bulk resin blends containing 20% DDM-BMI compared with 110 J/m^2 for pure DCBA [9]), their use temperature is limited by the T_g

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[*] Corresponding author. Tel.: +44-1483-259587; fax: +44-1483-876851.
E-mail address: i.hamerton@surrey.ac.uk (I. Hamerton).

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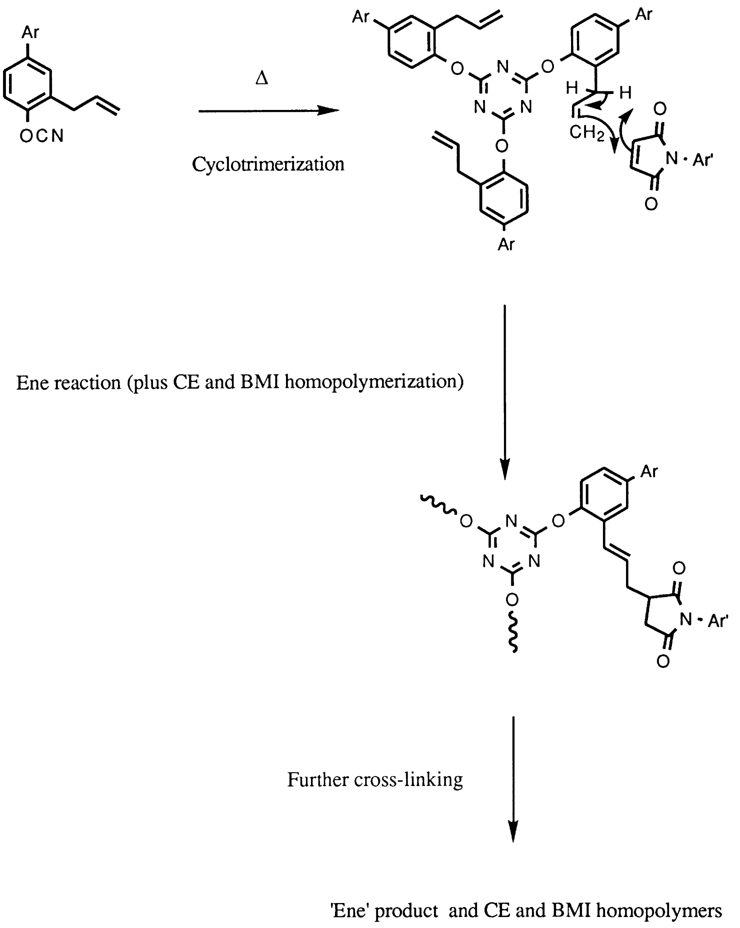


Proposed mechansim of allyl-functionalized cyanate ester/*bis*-maleimide co-reaction

Scheme 1.

of the polycyanurate network (dry T_g = 230–290°C depending on DDM-BMI content in the blend [1]).

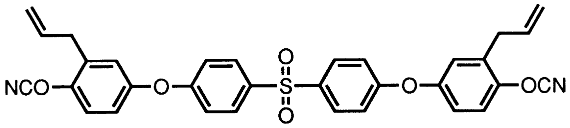
One approach to solving this problem has been the development of special reactive “modifiers” which have the ability to react with both homopolymer networks. The mechanism by which the co-reaction occurs when allyl-functionalised CEs are involved is believed to be via an ‘ene’ mechanism which follows the initial cyclotrimerisation reaction [7,10–14] (Scheme 1, proposed mechanism of allyl-functionalised cyanate ester/bismaleimide co-reaction, after Refs. [7,12]; Ar and Ar$'$ represent aromatic backbones). In the case of CEs bearing a propenyl group, the co-reaction is believed to proceed via a Diels–Alder route and work is currently underway to confirm this experimentally [15]. The addition of a small amount of the reactive modifiers reported in this work to a CE/BMI blend may increase the T_g of the overall network by linking the polycyanurate network to the higher T_g poly(BMI) network, whilst retaining much of the original morphology of the blend and thus retaining the high fracture toughness.

We have already reported [13,14,16] the preparation and thermal characterisation of the alkenyl-functionalizsd aryl cyanate esters and the present publication deals with assessment of the mechanical properties of these polymeric matrices when applied to carbon-fibre reinforced composite samples. It is envisaged that these materials may be used as reactive viscosity/toughness modifiers in formulations containing monomers which may be inherently brittle, or require modification of their viscosity to facilitate processing. Work continues to examine this potentially fruitful area of materials chemistry.

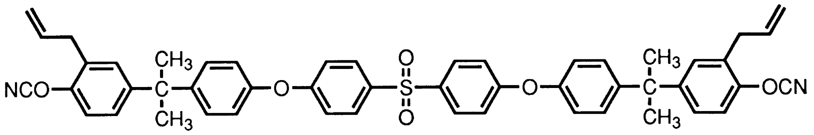
2. Experimental

2.1. Materials

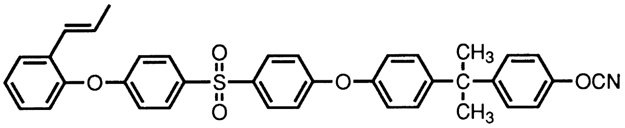
The preparations of the allyl- (4rOCN and 6rOCN) and propenyl- (4rPOCN and 5rPOCN) functionalised CEs studied in this work (Fig. 1) have already been reported



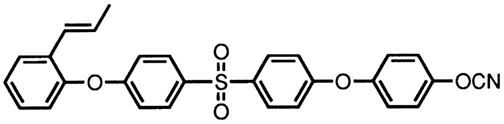
4rOCN



6rOCN



5rPOCN



4rPOCN

Fig. 1. Structures of the modifiers studied in this work.

elsewhere [13,14,16]. The composite matrices were based on two commercially available materials: one, a low molecular weight (30% reacted) prepolymer of bisphenol A dicyanate, DCBA and the other a commercially available low melting point blend of three BMI components. The latter comprised *bis*(4-maleimidophenyl)methane, 2,4′-*bis*-maleimidotoluene and 1,6′-*bis*-maleimido-2,2,4-trimethylhexane blended in an approximate ratio of 55:30:15 and this blend is designated ‘BMI’ in the remainder of this work. All samples of blends were catalysed with copper(II) naphthenate (300 ppm Cu^{2+} by weight) and 4 parts per hundred (phr) nonylphenol. The modifiers were first melt blended at approximately 80°C then catalyst and acetone (approximately 100 cm^3 per 80 g resin) were added. Table 1 details the composition of the blends tested in this work. The following convention is adopted: the component is prefixed by the weight% composition e.g. a resin blend containing 50%

Table 1
Blends compositions used in test samples in this study (all blends contained 300 ppm Cu^{2+} and 4 phr nonylphenol)

Blend designation	% DCBA (by weight)	% BMI	% 4rOCN	% 4rPOCN	% 5rPOCN	% 6rOCN
50DCBA-50BMI	50	50	0	0	0	0
65DCBA-35BMI	65	35	0	0	0	0
80DCBA-10BMI-10(4r)	80	10	10	0	0	0
70DCBA-20BMI-10(4r)	70	20	10	0	0	0
50DCBA-35BMI-15(4r)	50	35	15	0	0	0
35DCBA-35BMI-30(4r)	35	35	30	0	0	0
50DCBA-35BMI-15(4rP)	50	35	0	15	0	0
50DCBA-35BMI-15(5rP)	50	35	0	0	15	0
35DCBA-35BMI-30(5rP)	35	35	0	0	30	0
80DCBA-10BMI-10(6r)	80	10	0	0	0	10
70DCBA-20BMI-10(6r)	70	20	0	0	0	10
50DCBA-35BMI-15(6r)	50	35	0	0	0	15
35DCBA-35BMI-30(6r)	35	35	0	0	0	30

DCBA, 35% BMI and 15% 4rOCN is denoted blend [50DCBA-35BMI-15(4r)] and so on.

2.2. Preparation of carbon-fibre prepreg samples

An epoxy sized fibre (Toray T800HB) was chosen as the reinforcing fibre for the composite samples. The resins were solution impregnated onto the fibre using a drum-winding type pre-pregger. Composite lay up involved the preparation of 10-ply unidirectional laminates for the majority of the mechanical tests, although in the case of double cantilever beam fracture toughness (G_{IC}) test specimens, 18-ply laminates were prepared (a PTFE film insert was placed between plies 9 and 10 prior to cure to produce a laminate specimen containing a pre-initiated crack).

2.3. Curing of carbon-fibre prepreg samples

Pre-impregnated carbon-fibre (prepreg) was prepared using a dip-winding technique (Toray T800HB fibre, an epoxy-sized 6K filament/tow fibre was used — a common reinforcement for BMI and epoxy prepreg/composite systems). The fibre was passed through a bath containing the resin before being wound onto a drum coated in release paper. The resins and modifiers (ca. 70 g total) in the appropriate ratios were first melt blended in a beaker on a hot-plate stirrer at 80°C. The heat was turned off and immediately acetone was added carefully to bring the total volume to ca. 150 cm^3. The catalyst mixture (pre-mixed) was added in the appropriate amount and stirred in thoroughly; the resin solution was then used within 24 h.

All laminate samples were cured in an autoclave comprising a flat metal bed plate protected by a sheet of ‘Melanex’ PTFE film. Layers of non-porous PTFE film (from which the backing paper had been previously removed) were placed above and below the laminate stack, in order to retain the resin within the laminate as it passed through its lowest viscosity stages. A caul plate, of dimensions just smaller than the prepreg stack, was next placed on the non-porous PTFE, serving to maintain an even application of pressure and hence preventing the laminate panel from warping during cure. Porous PTFE was then placed over the caul plate to bleed excess resin from the stack. A vacuum was applied via a braided metal line running into a vacuum bag which enveloped the entire stack. A tight seal was ensured by sealing down the edges with tape. Early application of the vacuum served to remove any volatiles from the prepreg and also retained the stack in place on the bed plate as the vacuum bag shrank to a tight fit. The efficient application of a vacuum into the stack, and transport of excess resin and volatiles out, was achieved by a breather cloth placed directly below the inner surface of the vacuum bag.

The following cycle was then applied: a ramp of 1 K/min was initiated from room temperature to 220°C and a vacuum applied and held overnight (approximately 16 h). A pressure of 100 psi was gradually applied in the autoclave at the beginning of the heating cycle and was held throughout. The heating cycle was interrupted and held isothermally for 1 h (70°C in the case of the blends containing 4rOCN and 90°C in the case of those containing 6rOCN) before being reheated to a maximum cure temperature of 220°C. As the pressure in the autoclave reached 30 psi the vacuum was vented. After the heating phases, the stack was cooled at 3 K/min to 65°C and the cured laminate panel released from the bed plate. A free standing post cure comprising a minimum of 3 h at 220°C was applied to all panels. Table 1 shows the composition of the composites.

2.4. Analysis of cured polymer blend and carbon-fibre composite samples

2.4.1. Measurements

DMTA was performed at a heating rate of 4 K/min under nitrogen (40 cm^3/min) using a Polymer Laboratories Mk II DMTA. 10-Ply unidirectional laminates (ca. $30 \times 10 \times 2$ mm^3) were tested in dual cantilever bending mode at a fixed frequency of 10 Hz between 30 and 300°C. The T_g value (denoted T_g onset) was taken from the tangents of the E' curves at the point at which the modulus decreases, although the tan δ value is also given. The standard post-cure schedule selected for composites was 3 h at 220°C in a circulating air oven (in the same manner as the neat resin samples).

With the exception of the G_{IC} measurements, all of the mechanical tests described were carried out on Instron (models 1185 and 1122) screw-driven mechanical testing machines giving the data in the form of load/deflection graphs. Interlaminar shear strength (ILSS) data were obtained using the following test conditions loading roller diameter (dia.) of 10 mm, support rollers of dia. = 6 mm, span between support rollers = 10 mm, for five rectangular 10-ply unidirectinal laminate samples ($20 \times 10 \times$ ca. 2 mm^3). The crosshead speed was 1 mm/min. Flexural tests were carried out on five rectangular 10-ply unidirectional laminate samples ($120 \times 10 \times$ ca. 2 mm^3) using a loading roller dia. = 25 mm, support rollers dia. = 10 mm, span between support rollers = 80 mm. The crosshead speed was 5 mm/min. For compression test measurements, five Celanese-type specimens [17] were prepared from 10-ply unidirectional laminates (incorporating a 10 mm test section). The crosshead speed was 2 mm/min.

The double cantilever beam (DCB) test sample for G_{IC} fracture toughness measurements (of crack propagation) was prepared according to the CRAG procedure [17] and measurements were carried out on an Instron 4301 screw-driven machine. (dimensions $150 \times 20 \times 3$ mm^3) with a pre-initiated crack of 40 mm. Brass hinges were attached to the surfaces of the sample in order that the sample crack could be propagated. A crosshead speed of 0.5 mm/min was used. Readings of crack growth rate were taken at the initial crack propagation, at 1 mm intervals for the first 10 mm, and at 5 mm intervals up to a total crack length of 40 mm.

Scanning electron micrographs (SEMs) were obtained on an Hitachi S-450 scanning electron microscope with an accelerating voltage of 20 kV. Composite fracture surfaces were coated with gold and palladium prior to analysis.

The density of both the cured neat resins and laminate samples was determined using a British standard method (BS 2782 pt 6 method 620A) involving the Archimedes principle (weighing the samples in air and water). Ultrasound tests (C-scans) were carried out on the cured laminate samples in order to detect defects in the composite, at the time it was not possible to detect microvoid content. In all cases, only good laminates (with no detectable flaws and acceptable fibre content values: Table 4) were used in subsequent mechanical tests. Owing to the variation in fibre volume (V_f) obtained for some of the samples tested, some of the mechanical properties (Mp) were normalised to an idealised fibre volume fraction of 60% using the following relationship:

$$M_p \text{ (normalised)} = 60\, M_p/V_f(\%). \quad (1)$$

3. Results and discussion

3.1. Dynamic mechanical thermal analysis (DMTA) of neat resin samples

The DMTA data for the neat resin samples are presented in Table 2. Unless otherwise stated, all T_g values discussed in the text refer to T_g (onset).

3.1.1. Unmodified neat resins

The neat resin samples of DCBA and BMI were subjected to free-standing postcure of 4 h at 250°C and DMTA analysis revealed that the resulting polycyanurate of DCBA displayed a T_g of 260°C (Fig. 2a) and the poly(BMI) a T_g of 430°C (Fig. 2b), although the latter was ill-defined as the sample must inevitably be undergoing the onset of thermal degradation during the later stages of the scan. The blend [65DCBA-35BMI] was chosen as a suitable example against which subsequent, modified blends might be assessed. DMTA analysis of neat resin samples of [65DCBA-35BMI] after two different post cure schedules had been employed (Fig. 2c and d) revealed that the resulting polymer displayed two values of T_g (this is particularly evident when the tan δ data are considered as the second, higher temperature transition appears as a shoulder on the first). After postcure at the higher temperature the lower transition, thought to be due to the undercured polycyanurate component of the blend, was observed to move to a higher temperature (and correspond more closely with the T_g value recorded for DCBA (Fig. 2a). This phenomenon was also observed in several of the other plots, although in all cases the higher transition is truncated as the blend was beginning to undergo decomposition at this temperature, yielding degradation products and necessitating the conclusion of the analysis. The DMTA data for the unmodified blend do suggest the formation of an IPN, or perhaps a polymer blend comprising large, discrete domains of polycyanurate and poly(BMI).

3.1.2. Modified neat resins

In order to rationalise the data, the figures depict the DMTA traces of the blends containing different concentrations of a given modifier to demonstrate the effect of loading on the dynamic mechanical properties. When blends containing different modifiers are discussed, then the discussion is limited to blends containing the same DCBA:BMI:-modifier ratio.

For the blends containing the 4rOCN modifier the DMTA data (Fig. 3) resemble those of the DCBA homopolymer in that they display a single tan δ peak (unlike [65DCBA-35BMI]). Blend [70DCBA-20BMI-10(4r)] displays a slightly lower value of T_g than the higher loading blend [70DCBA-20BMI-15(4r)]. In both cases the damping (tan δ) peak is slightly broader than the DCBA homopolymer.

The blends containing the 6rOCN modifier, [80DCBA-10BMI-10(6r)], [70DCBA-20BMI-10(6r)]

Table 2
Mechanical properties of neat resin specimens (all neat resin blends were subjected to a final postcure of 250°C for 4 h)

Sample designation	T_g (onset)	T_g (tan δ)	K_{IC} (MN/m$^{3/2}$)	G_{IC} (J/m^2)	E_f (GPa)
DCBA	260	280	0.68	112	3.62
BMI	430	–[a]	–[a]	11	–[a]
50DCBA-50BMI	220	250	0.51	54	4.29
65DCBA-35BMI	225	255	0.70	105	4.03
80DCBA-10BMI-10(4r)	246	283	0.63	102	3.43
70DCBA-20BMI-10(4r)	254	279	0.68	111	3.65
50DCBA-35BMI-15(4r)	234	272	0.62	83	4.05
50DCBA-35BMI-15(4rP)	233	263	0.64	88	4.08
50DCBA-35BMI-15(5rP)	226	251	0.71	108	4.04
80DCBA-10BMI-10(6r)	246	272	0.66	110	3.48
70DCBA-20BMI-10(6r)	241	264	0.73	126	3.72
50DCBA-35BMI-15(6r)	245	271	0.58	73	4.07

[a] Not measured.

and [50DCBA-35BMI-15(6r)], displayed similar values of T_g to the DCBA homopolymer, albeit with slightly broadened tan δ peaks. Interestingly, there is a distinctly bimodal tan δ trace in [70DCBA-20BMI-10(6r)], suggesting a degree of heterogeneity in this particular blend (Fig. 4b), although it is not immediately apparent why this should be so. The blends containing the propenyl-based modifiers (4rPOCN and 5rPOCN) yielded resins with lower values of T_g than the DCBA homopolymer. This was particularly true of [50DCBA-35BMI-15(5rP)], but less marked for [50DCBA-35BMI-15(4rP)]. The lower T_g values may reflect the increased flexibility of the modifiers and their lower functionality ($f = 2$) than the corresponding allyl-based modifiers (4rOCN and 6rOCN), $f = 4$, leading to a lower crosslink density in the final resin network. Both DMTA traces appear very similar in their profiles (Fig. 5).

3.2. Mechanical properties (E_f, G_{IC} and K_{IC}) of neat resin samples

The DCBA homopolymer is relatively tough ($K_{IC} = 0.68$ MN/m$^{3/2}$, $G_{IC} = 112$ J/m^2) and the BMI inherently brittle ($G_{IC} = 11$ J/m^2). By forming a blend (IPN) of these two components, it is possible to raise the fracture toughness significantly, but only truly when the DCBA is in excess (Table 2). For example, [65DCBA-35BMI] yields one of the toughest blends tested in this study ($K_{IC} = 0.70$ MN/m$^{3/2}$, $G_{IC} = 105$ J/m^2). If one considers the effect of each modifier in turn, in general, as with the unmodified polymers [9], blends containing higher CE contents yield higher K_{IC} and G_{IC} values. For example, at 15% incorporation (to maintain a BMI loading of 35% by weight) then it is apparent that the following order of fracture toughness is observed:

[50DCBA-35BMI-15(5rP)] > [50DCBA-35BMI] > [50DCBA-35BMI-15(4rP)] > [50DCBA-35BMI-15(4r)] > [50DCBA-35BMI-15(6r)].

The toughest of the modified neat resins tested here was blend [70DCBA-20BMI-10(6r)] ($K_{IC} = 0.73$ MN/m$^{3/2}$, $G_{IC} = 126$ J/m^2). However, in order to assess the full impact of this combination, it would have been necessary to test an unmodified blend comprising [80DCBA-20BMI] and this was not undertaken. Clearly, the propenyl-based modifiers may develop lower crosslink

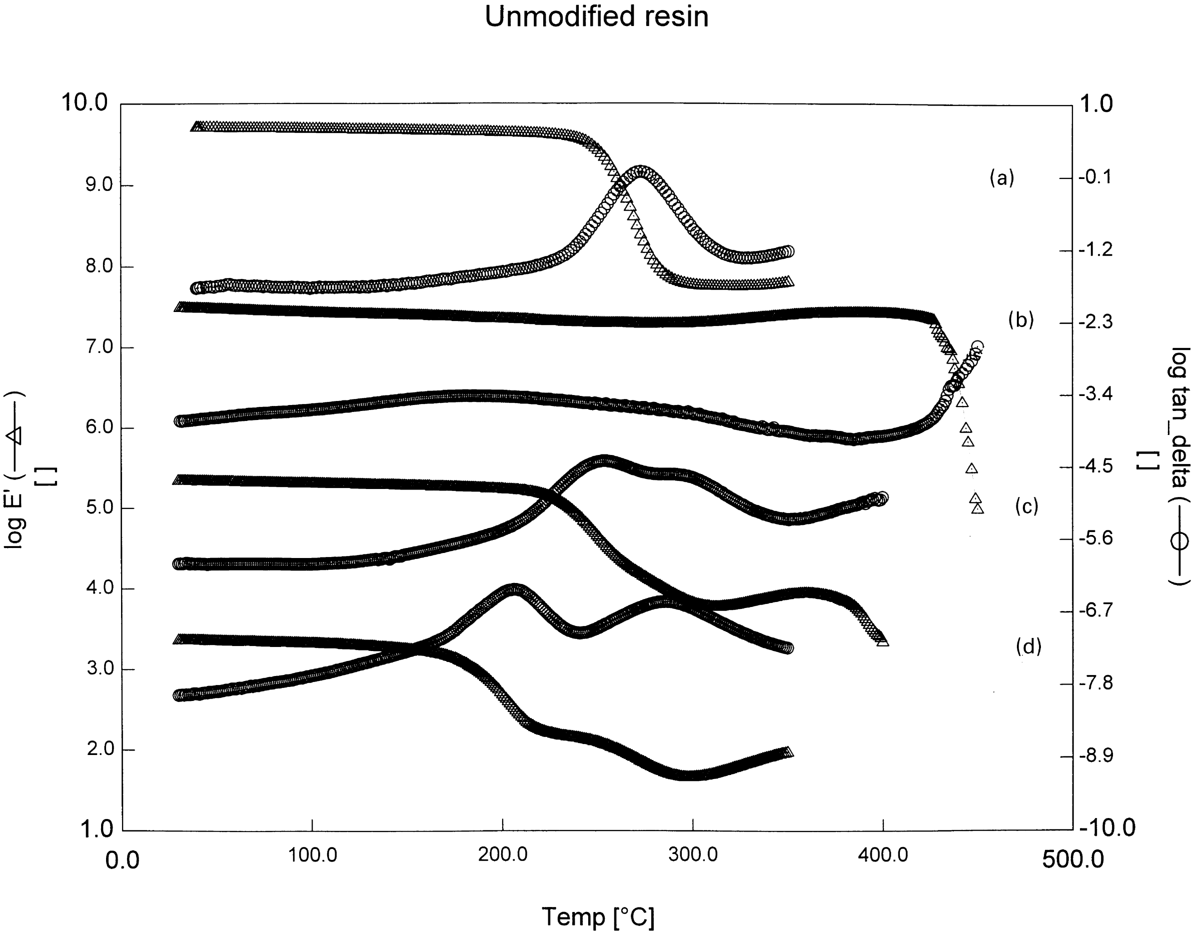


Fig. 2. DMTA data (dual cantilever bending mode, 4 K/min under nitrogen, 10 Hz) showing the dynamic mechanical properties of the cured neat resin samples of the homopolymers of: (a) DCBA, and (b) BMI and of an unmodified blend [65DCBA-35BMI] after postcure at (c) 250, and (d) 220°C.

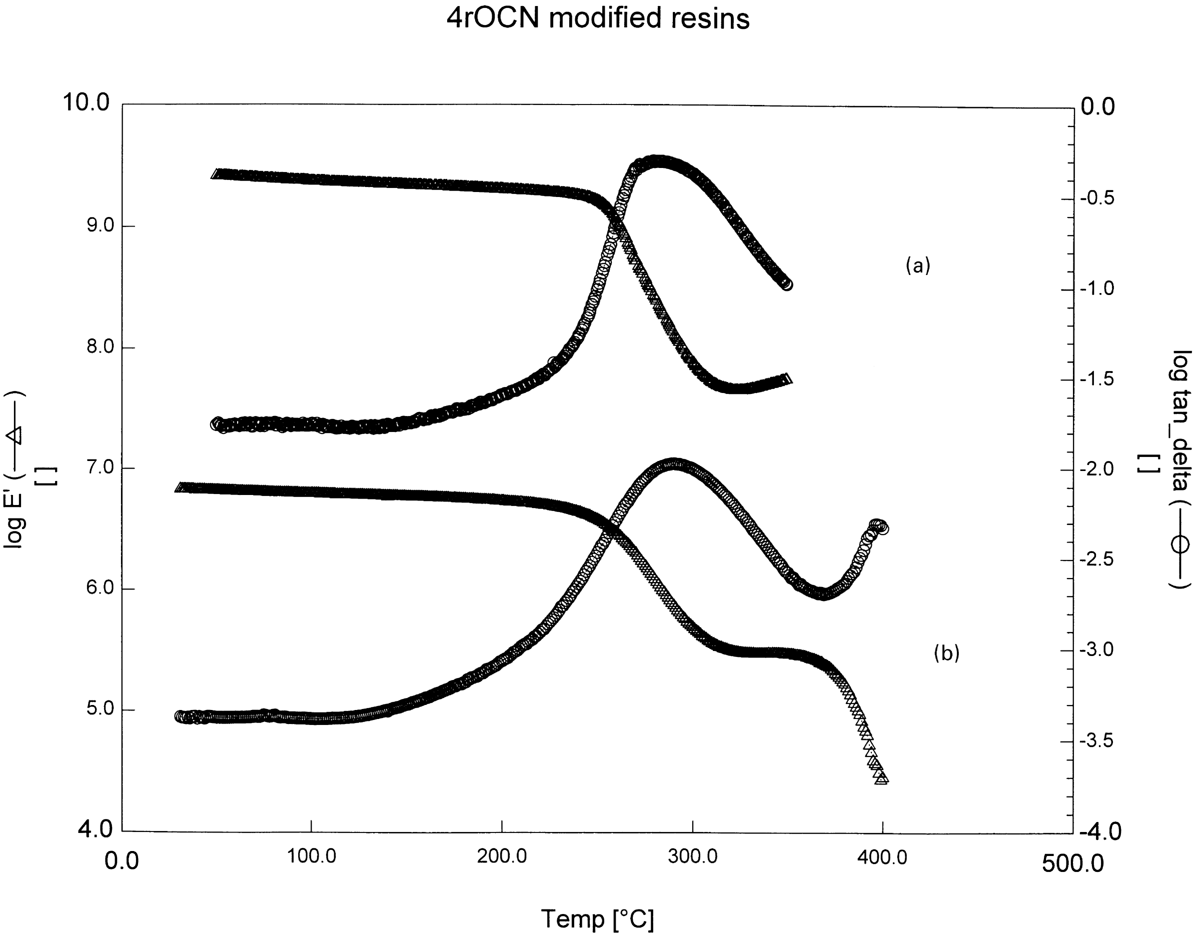


Fig. 3. DMTA data (dual cantilever bending mode, 4 K/min under nitrogen, 10 Hz) for cured neat resin blends containing the 4rOCN modifier: (a) [70DCBA-20BMI-10(4r)] and (b)[50DCBA-35BMI-15(4r)].

densities in the cured networks than their allyl-based counterparts, presumably enhancing the fracture toughness for a given level of incorporation.

In summary, the data in Table 2 demonstrate that it is possible to produce a number of modified DCBA-BMI neat resin blends with superior mechanical properties (in terms of K_{IC}, G_{IC} and flexural modulus, E_f) to the unmodified [65DCBA-35BMI] standard blend. It should be further noted that while [50DCBA-50BMI] dsiplays the highest value of E_f (4.29 GPa) it has a correspondingly low value of G_{IC} (54 J/m^2) and although the value of T_g is relatively high for DCBA (280°C), it yields a relatively low value of E_f (3.62 GPa).

3.3. Dynamic mechanical thermal analysis (DMTA) of composite samples

The DMTA data for composite samples are presented in Table 3. Unless otherwise stated, all T_g values discussed in the text refer to T_g (onset).

3.3.1. Unmodified composite blends

After the cure schedule (3 h at 180°C + 2 h at 220°C) the composite sample containing blend [50DCBA-50BMI] displayed a T_g of 165°C. This value was considerably lower than that recorded for the corresponding neat resin slab (i.e. T_g = 220°C after 6 h at 220°C + 2 h at 250°C), but the composite sample had experienced a lower final post-cure temperature than the neat resin. The composite sample containing blend [65DCBA-35BMI] was selected as a 'standard' baseline sample for comparative purposes and after the following cure schedule (3 h at 180°C + 3 h at 220°C) a T_g of 165°C was recorded, this value rose to 220°C after a free-standing postcure of 4 h at 250°C was applied. However, in order to present a truly comparative study, all subsequent modified composite samples were subjected to the 'standard' cure schedule (omitting the 250°C postcure). This decision was taken in order to examine the effects of the modifiers during a light cure schedule.

3.3.2. Modified composite samples

For each modifer loading, the following trends in T_g were

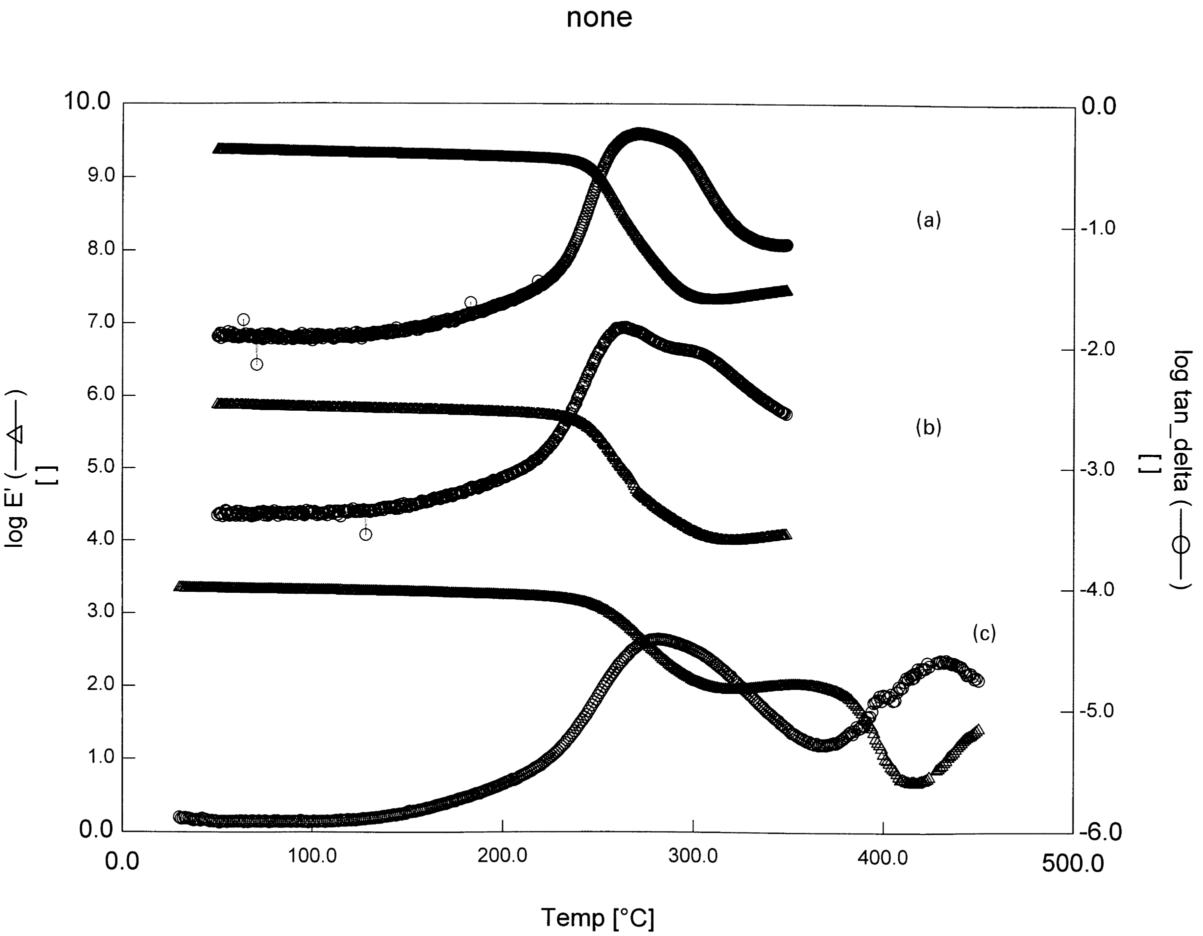


Fig. 4. DMTA data (dual cantilever bending mode, 4 K/min under nitrogen, 10 Hz) for cured neat resin blends containing the 6rOCN modifier: (a) [80DCBA-10BMI-10(6r)], (b) [70DCBA-20BMI-10(6r)], and (c) [50DCBA-35BMI-15(6r)].

observed: at the highest level of modifier loading:

[35DCBA-35BMI-30(4r)] $>$ [35DCBA-35BMI-30(6r)] $\approx$ [65DCBA-35BMI] $\gg$ [35DCBA-35BMI-30(5rP)].and at the lower modifier concentration: [50DCBA-35BMI-15(4r)] $\gg$ [50DCBA-35BMI-15(6r)] $>$ [50DCBA-35BMI-15(5rP)] $>$ [65DCBA-35BMI].

Notably, [50DCBA-35BMI-15(4r)] gave the highest value of T_g of the samples tested here ($T_g = 190$°C), presumably reflecting the highest crosslink density, due to the relatively short chain length. The lower molecular weight of this modifier may also be a contributory factor, since a given weight of 4rOCN will contain more reactive functional groups than e.g. 6rOCN, also leading to a higher crosslink density. It is also worthy of note that the 4rOCN system has been shown [13,14] to be the most reactive of the modifiers (as a homopolymer) as evidenced by DSC. All things being equal, this would presumably lead to a higher degree of polymerisation for a given composition and cure schedule.

In summary, the rationale for incorporating pendant alkenyl groups on the CE modifiers was to allow them to co-react with the BMI network. Theoretically, a simple mixture of DCBA and BMI should give an IPN when cured in the same manner as that postulated for the commercial Skylex®BT resin with the polycyanurate and polymaleimide networks interpenetrating, but not chemically bonding together. The presence of the modifier serves to co-react with both networks producing a linked interpenetrating network (LIPN). A two-component IPN sometimes displays two distinct glass transitions by DMTA, one for each of the component homopolymers, and is consistent with the premise that the cured resin contains discrete regions of polycyanurate and poly(BMI) (and also interfacial regions where both are present) which undergo glass transitions at different temperatures. In order to examine the possibility of heterogeneity in these blends, after fracture, both neat resin and composite specimens were analysed using SEM. SEMs were similar for all neat resin samples and did not reveal the presence of phase separation (which may be discerned in the case of thermoplastic-modified CE systems [18]) although the inability to detect distinct phases may be due to the relative insensitivity of the method towards features on this scale. It is interesting to

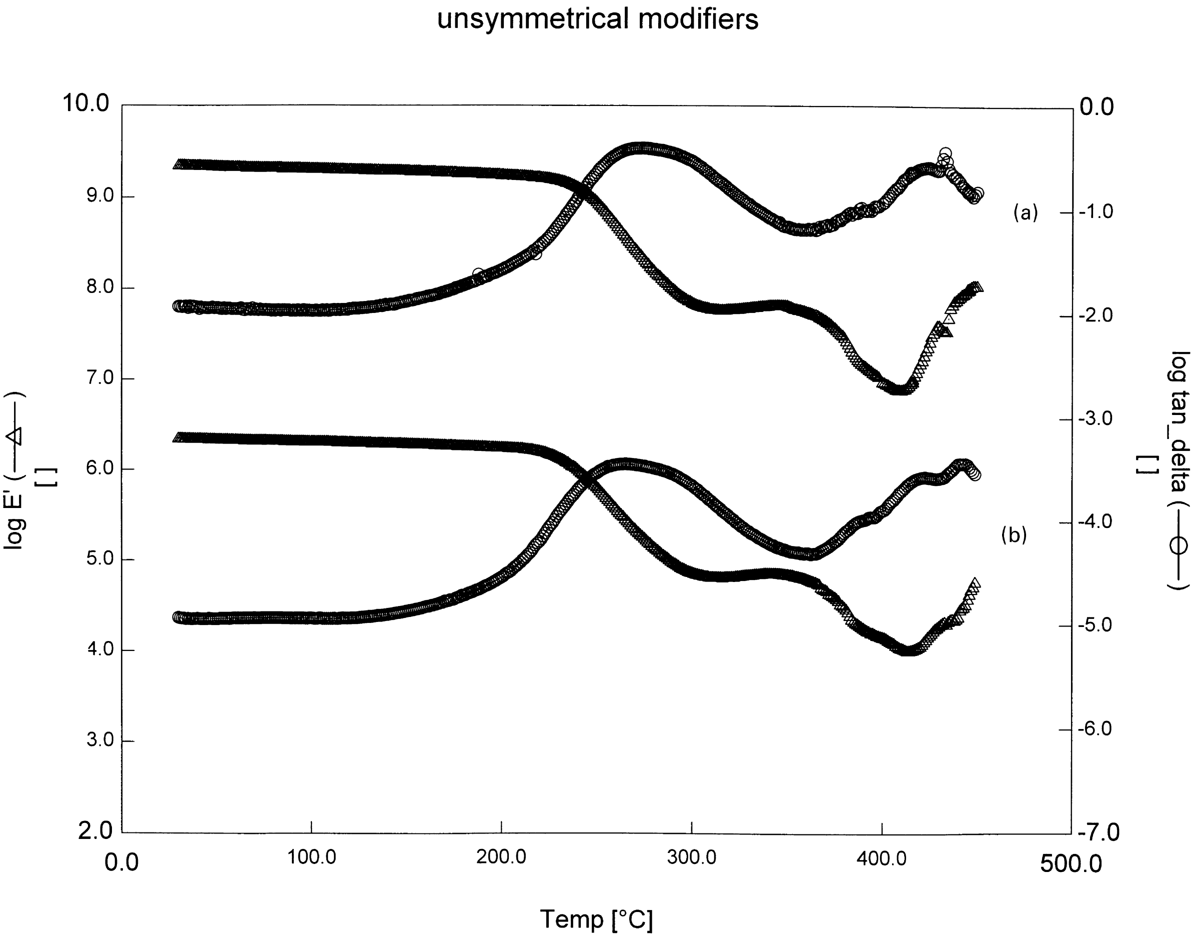


Fig. 5. DMTA data (dual cantilever bending mode, 4 K/min under nitrogen, 10 Hz) for cured neat resin blends containing the propenyl-based modifiers: (a) [50DCBA-35BMI-15(4rP)], and (b) [50DCBA-35BMI-15(5rP)].

note that the fibre–resin adhesion in composite samples was reasonably good as pieces of resin can be seen on the surfaces of the fibres in some cases (Fig. 6).

Dual glass transitions have been observed for DCBA/DDM-BMI blends [7] and some care must be taken in attempting to assign them to the polymerisation of a particular component as the kinetics of both cure processes (and the network development) may be affected by the presence of the second component. The homopolymerisation reaction of each component is probably being retarded in the presence of the other; a not unreasonable assumption. Lin and co-workers have already reported similar phenomena in compatible simultaneous IPN formed from bisphenol A diglycidyl ether (BADGE) and acrylics [19,20]. In their studies they reported that hydrogen bonding between the components (evidenced by infrared measurements) reduced BADGE chain mobility slightly leading to mutual entanglement between the two components. Lin et al. suggested that this network interlock effect provided a sterically hindered environment for the polymerisation reactions and led to lower rate constants and slightly higher activation energies than those observed during polymerisation of each of the single components.

On the basis of the DMTA results we believe that initially (under lighter cure schedules) the higher T_g is that of the DCBA component and the lower one due to the undercured poly(BMI) network. For samples post-cured at 250°C, the BMI cures to a greater degree, thus leading to a higher T_g; in general, the lower of the T_gs will govern the use temperature of the material. The effect of the modifier remains essentially the same in both cases, in that it increases the overall T_g by linking the part of the network with the lower T_g

Table 3
T_g values of carbon-fibre composite specimens from DMTA (after 220°C postcure) (all blends comprised 10-ply unidirectional laminates prepregged on T-800HB fibre)

Sample	T_g (onset)	tan δ_{max}
50DCBA-50BMI	165	190
65DCBA-35BMI	165	190
50DCBA-35BMI-15(4r)	190	225
35DCBA-35BMI-30(4r)	175	255 (ill-defined)
50DCBA-35BMI-15(5rP)	170	200
35DCBA-35BMI-30(5rP)	145	250
50DCBA-35BMI-15(6r)	175	203
35DCBA-35BMI-30(6r)	165	200

(whether it is polycyanurate of polyBMI) to the part with the higher T_g. With only one exception [70DCBA-20BMI-10(6r)], only one T_g was noted in blends containing modifiers (and usually this single T_g was higher than the first T_g of the unmodified blend).

3.4. Mechanical measurements for composite samples

3.4.1. G_{IC} measurements of composite samples

The G_{IC} data (Table 4) must be treated carefully in view of the variation in fibre content, V_f, as ideally, comparisons should be made between samples of near-identical V_f. The authors are aware that variations in V_f between samples can, in turn, lead to considerable variation in some composite properties. Consequently, the G_{IC} values (and the other composite mechanical data) were normalised to an idealised 60% V_f prior to comparison. Fortunately, the G_{IC} values obtained here for the unmodified blends were very similar in the order of magnitude to those obtained in earlier work [21] using very similar blends and sample types, but with V_f of ca. 60%. The similarity of the results suggests that the effect of the low fibre content in the unmodified blends may be limited in this particular case. For example, a 1:1 blend of DCBA/DDM-BMI was observed [9] to yield a 70% improvement in composite fracture toughness (G_{IC}) over an unmodified DCBA sample, i.e. the IPN formed in such a blend was inherently tougher than either of the component homopolymers. One possible explanation for the toughening mechanism is the formation of discrete polycyanurate and poly(BMI) regions (and mixed areas) in the IPN product. Discrete networks which were not chemically linked would give a limited increase in overall flexibility compared to a conventional crosslinked system and the observation of two T_gs (by DMTA) also suggests a degree of heterogeneity. Whatever the toughening mechanism, the effect of the modifiers is to link the two networks partially together. The DMTA data for the composite samples generally reveal in most cases only one T_g in blends containing modifiers (and usually this single T_g was higher than the first T_g of the unmodified blend).

It is important to compare normalised sample values and blends containing the same quantity of modifier. Hence, for the mode I fracture toughness, the following trend was observed: [50DCBA-35BMI-15(5rP)] $\gg$ [65DCBA-35BMI-15(4r)] $\approx$ [50DCBA-35BMI-15(4r)] $>$ [50DCBA-35BMI-15(6r)]. At the higher modifier loading: [65DCBA-35BMI] $>$ [35DCBA-35BMI-30(6r)] $>$ [35DCBA-35BMI-30(4r)]. Interestingly, an increase in the loading of modifier 6rOCN appeared to lead to a significant decrease in the fracture toughness. While the fracture toughness recorded for blend [65DCBA-35BMI] was not an ideal measurement (in view of V_f), the similarity in the data with those published earlier [21] suggests that it is a reasonable basis for comparison.

Unfortunately, G_{IC} data are only available for the blend [65DCBA-35BMI-15(5rP)] (Table 4) as laminate test

Table 4

Mechanical data (data normalised for composite fibre content to 60% V_f) for 10-ply (G_{IC} measurements performed on 16-ply laminates with the following fibre volumes) unidirectional carbon-fibre laminates

Sample	Fibre volume V_f (%)	Density ρ_c (g/cm^3)	Interlaminar shear stength (σ) (MPa)	Flexural strength, f_F (σ) (GPa)	Flexural modulus, E_f (σ) (GPa)	Compressive strength, F_{LC} (σ) (GPa)	Mode I fracture toughness, G_{IC} (σ) (J/m^2)	Normalised to 60% V_f
65DCBA-35BMI	33	1.47	104 (6)	1.89 (0.27)	133 (11)	1.06 (0.11)	372 (50)^a	620
50DCBA-35BMI-15(4r)	40	1.49	115 (2)	1.94 (0.23)	161 (14)	1.20 (0.04)	367 (52)^b	355
35DCBA-35BMI-30(4r)	54	1.58	101 (4)	2.03 (0.09)	135 (11)	1.00 (0.15)	337 (114)^c	368
50DCBA-35BMI-15(5rP)	45	1.55	113 (5)	2.24 (0.36)	143 (1)	1.30 (0.08)	513 (90)^a	855
35DCBA-35BMI-30(5rP)	55	1.59	92 (5)	1.81 (0.04)	131 (4)	1.10 (0.06)	–^{d}	-
50DCBA-35BMI-15(6r)	45	1.52	113 (3)	1.88 (0.21)	125 (1)	1.17 (0.10)	346 (36)^e	494
35DCBA-35BMI-30(6r)	44	1.57	110 (7)	1.45 (0.09)	110 (2)	1.07 (0.16)	271 (30)^f	378

[a] $V_f >= 36\%$, $\rho_c = 1.48$ g/cm^3.

[b] $V_f = 62\%$, $\rho_c = 1.63$ g/cm^3.

[c] $V_f = 55\%$, $\rho_c = 1.60$ g/cm^3.

[d] Not measured.

[e] $V_f = 42\%$, $\rho_c = 1.49$ g/cm^3.

[f] $V_f = 43\%$, $\rho_c = 2.48$ g/cm^3.

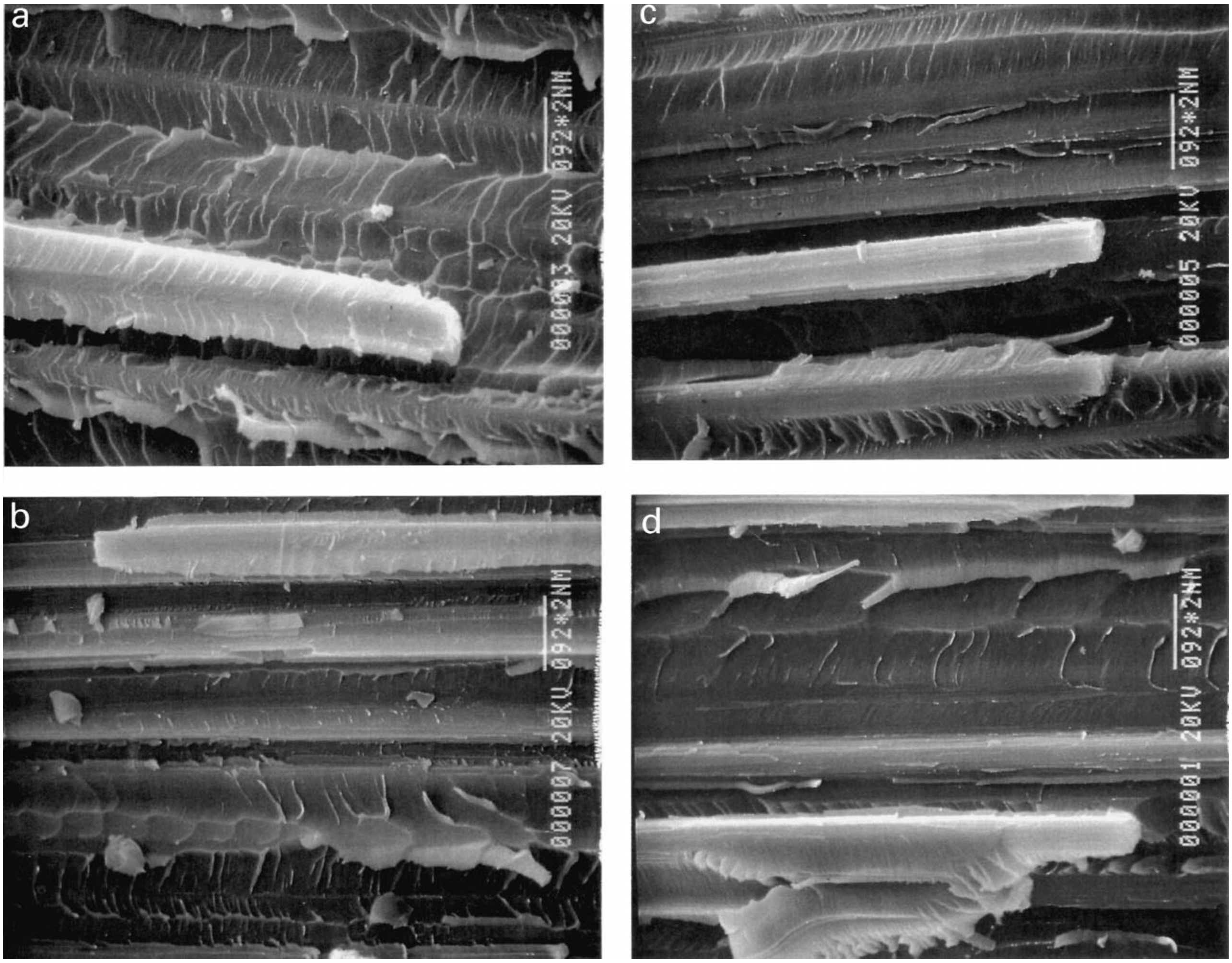


Fig. 6. Scanning electron micrographs (accelerating voltage of 20 kV) of fracture surfaces of 10-ply laminate samples of blend: (a) [65DCBA-35BMI], (b) [65DCBA-35BMI-15(4r)], (c) [50DCBA-35BMI-15(5rP)], and (d) [50DCBA-35BMI-15(6r)].

panels incorporating higher levels of 5rPOCN were unsuitable for analysis (due to excessive void formation, possibly as a result of the volatility of the modifier). The value of G_{IC} for blend [65DCBA-35BMI-15(5rP)] ($G >_{IC}=$ 513 J/m^2) is the largest obtained for the blends tested in the course of this work, significantly higher than both the unmodified blend [65DCBA-35BMI] and also blends containing the symmetrical modifiers 4rOCN and 6rOCN. The G_{IC} figure recorded here for [65DCBA-35BMI-15(5rP)] is even superior to that reported by Mackenzie and Malhotra ($G_{IC} = 340$–500 J/m^2) for thermoplastic polyethersulphone-modified CE resin composites (954-2A) [6]. If one compares the neat resin and composite samples (Tables 2 and 4), where data exist for both specimens and where the loading of modifier is constant (e.g. at 15% by weight), the following observations may be made. There does appear to be a similar trend in fracture toughness in that the same order is apparent:

[50DCBA-35BMI-15(5rP)] > [65DCBA-35BMI] >
[50DCBA-35BMI-15(4r)] > [50DCBA-35BMI-15(6r)].

This suggests that the fine neat resin fracture toughness properties exhibited by the modified blends (and particularly those incorporating 5rPOCN are translated into the corresponding composite.

3.4.2. Interlaminar shear strength (ILSS) measurements

Data from ILSS tests (normalised to 60% V_f) are shown in Table 4. It can be seen from Table 4 that there is often a variation in V_f between different samples, but as ILSS measurements are not highly dependent on fibre volume fraction [17], they may provide a better comparison of the different resins than those tests which are highly V_f dependent. There are subtle variations observed in the data presented, but no great variation in the value of ILSS recorded over the standard blend [65DCBA-35BMI], the highest being recorded for [50DCBA-35BMI-15(4r)] (115 ± 2 MPa). A general observation worth noting is that the modifiers to yield higher values of ILSS at the lower (15% level of incorporation) in each case. The failures in these test specimens could have occurred either at the fibre–resin interface, or in the matrix itself as the actual failure modes were not investigated, either mechanism could be a possibility.

3.4.3. Flexural modulus (E_f) and flexural strength (f_F) measurements

Owing to the aforementioned variation in V_f for some of the samples tested, normalised flexural strength data are presented in Table 4 in order that a direct comparison between samples might be made and [65DCBA-35BMI] is again offered as a baseline. The incorporation of the modifier 4rOCN leads to the highest flexural strengths and moduli of those measured, although the variation is not great. In contrast to the ILSS data, a general observation with the modifiers is that 30% incorporation does appear to offer a slight advantage over 15% incorporation, giving slightly higher values of flexural strength in both cases.

3.4.4. Compressive strength (F_{LC}) measurements

Table 4 contains the normalised data from the measurements of compressive strength. Again it is apparent that blend [50DCBA-35BMI-15(4r)] gave the highest compressive strength of 1.20 ± 0.04 GPa. It is apparent that there is a somewhat larger distribution in the F_{LC} data than for other tests, although the reason for this is not immediately apparent. Composites incorporating modifier 6rOCN displayed normalised compressive strengths lower than those of blend [65DCBA-35BMI] (1.06 ± 0.11 GPa). A general observation with the modifiers is that 30% incorporation appears to offer little advantage over 15% incorporation, giving slightly lower values of compressive strength in both cases. Again it is apparent that both blends incorporating the modifier 5rPOCN gave compressive strengths greater than the unmodified. In common with the symmetrical analogues 4rOCN and 6rOCN it is observed that incorporation of 30% 5rPOCN appears to offer little advantage over 15%, giving slightly lower values of compressive strength in both cases.

3.5. Summary of mechanical data

It is accepted that from Table 4, there are some variations in data from some of the mechanical tests and normalisation was applied to allow valid comparison between samples. However, it is worth noting that these composites were made on a very small scale, using processing methods that could not be optimised due to the small (laboratory-scale) quantities of the novel reactive modifiers produced. Hence, the development of the methodology was very much an ongoing process and the conditions used to process later samples were probably better than for the earlier ones. Unfortunately, within the context of a PhD research programme it was not possible to repeat all of the earlier work using the later processing conditions to achieve smaller variations in the data. As such, the composite tests demonstrate the potential of the experimental materials, rather than an absolute measure of their composite properties.

Taken in this context, clearly the data presented in Table 4 indicate that it is possible to produce blend compositions which may be optimised for various mechanical properties by varying the modifier and the loading. For example, the use of the 4rOCN modifier may be incorporated to produce optimal values of T_g and ILSS and E_f, etc. However, the modifier 5rPOCN appears to offer the greatest all round potential for property modification. Table 5 presents selected mechanical data for blend [50DCBA-35BMI-15(5rP)] and the unmodified blend [65DCBA-35BMI]. These data demonstrate that incorporation of 15% 5rPOCN can yield optimal properties such as fracture toughness and glass transition temperature (when compared with the unmodified BMI/CE blend without leading to a degradation in other mechanical properties). This is a very encouraging finding in the further development of inherently tough, functionalised cyanate esters for incorporation into BMI networks effecting improvements in impact resistance whilst maintaining the high thermal stability of these materials. Work continues to examine the properties of this modifier and to optimise the processing conditions.

4. Conclusions

While two T_g values were noted in polymer blends containing commercial cyanate esters and bismaleimides, the addition of our modifiers yielded (in all but one case) a single T_g (the second, unobserved, transition possibly

Table 5
Mechanical properties of selected blends tested

Property	65DCBA-35BMI	50DCBA-35BMI-15(5rP)
ILSS[a] (MPa)	104	113
Flexural modulus[b] (GPa)	133	143
Flexural strength[b] (GPa)	1.89	2.24
Compressive strength[b] (GPa)	1.06	1.30
Fracture energy, G_{IC}, (J/m^2)	372	513
G_{IC}, (J/m^2) normalised to 60% V_f	620	855
T_g (composite, T_g onset), (°C)	190	170

[a] ILSS, interlaminar shear strength.

[b] Normalised to 60% fibre volume fraction.

competing with the thermal degradation process) and in these cases this value was higher than the first T_g of the unmodified blend. In general, ILSS values approximating to, or greater than, the unmodified blend were observed for the samples containing either 4rOCN or 6rOCN, while blends incorporating 15 and 30% 5rPOCN, respectively show values of ILSS similar to that of the unmodified blend. In general, the compressive strength of the composite blends decreased as the incorporation of the modifier was increased. The trend in fracture toughness properties recorded for neat resins was apparently translated into the corresponding composites. It is clear that incorporation of 15% 5rPOCN can yield optimal properties such as fracture toughness and glass transition temperature (when compared with the unmodified DCBA/BMI blend) without leading to a degradation in other mechanical properties. SEM did not give any indications of morphological changes, brought about by inclusion of the modifiers as no phase separation was observed.

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