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Mechanical properties of tough, high temperature carbon fibre composites from novel functionalized aryl cyanate ester polymers

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Carbon fibre pre-impregnated tape (prepreg) was prepared from a range of prepolymers comprising blends of propenyl-functionalized cyanate ester (CE) oligomers with commercial bis-maleimide (BMI) monomers. Cured neat resin plaques and carbon fibre composites were prepared by autoclave moulding. Various blends of a commercial BMI mixture, a CE and a co-monomer with either allyl or propenyl and cyanate pendant groups were prepared. Differential scanning calorimetry (d.s.c.) data were used to monitor cure of neat resin, while dynamic mechanical thermal analysis (d.m.t.a.) was used to assess cure cycles of composite materials by the measurement of glass transition temperatures (T_g). Composite properties measured were interlaminar shear strength, flexural strength, compressive strength and Mode 1 Fracture toughness (G_{IC}). Copyright © 1996 Elsevier Science Ltd.

(Keywords: cyanate esters; functionalized; composites)

INTRODUCTION

Bis-maleimides (BMIs) have been proposed[1] as potential replacements for epoxy resins (epoxies) in some high performance applications. The latter are used extensively[2] as polymer matrices in e.g., structural composites despite suffering from poor hot/wet performance a feature which limits the applications in which they may be used to non-thermally critical components. While BMIs cure (either thermally or in the presence of catalysts) to exhibit fine high temperature properties, they produce brittle thermoset products due to the high crosslink density of the network. The problems associated with the processing of the monomers and the toughness and impact-resistance of the resulting networks must be addressed if BMIs are to find increasing acceptance in this application. A number of approaches have been adopted to toughen BMIs, but the most common (upon which many commercial products are based) include chain extension of the prepolymer (e.g., by non-stoichiometric reaction with a nucleophile such as an aromatic diamine to form a maleimide-terminated, crosslinkable aspartimide[1,3] and co-reaction with an inherently tough comonomer such as an alkenyl-functionalized aromatic compound[4]. It has already been demonstrated[5] that the co-reaction between allyl-functionalized aryl cyanate esters (CEs) and BMI monomers produces network polymers with desirable features (high glass transition temperature, T_g, and thermal stability). CEs are becoming increasingly popular as matrices for composites[6] and a number of commercial systems are now available. In this publication we deal with the 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.

EXPERIMENTAL

Materials

All reagents and solvents were reagent grade quality, purchased commercially [with one exception, 2,2′-*bis*-(3-allyl-4-hydroxyphenyl)isopropylidene which was supplied by Ciba-Geigy, UK], and used without further purification unless otherwise noted. The preparation of the allyl-functionalized CE monomer, 2,2′-*bis*(3-allyl-4-cyanatophenyl)isopropylidene (structure shown in *Figure 1*), studied in this work has already been reported elsewhere[5a,b]. The commercial CE prepolymer AroCy® B-30 (B-30, monomer represented in *Figure 1*) was obtained from Hi-Tek Polymers (now part of the

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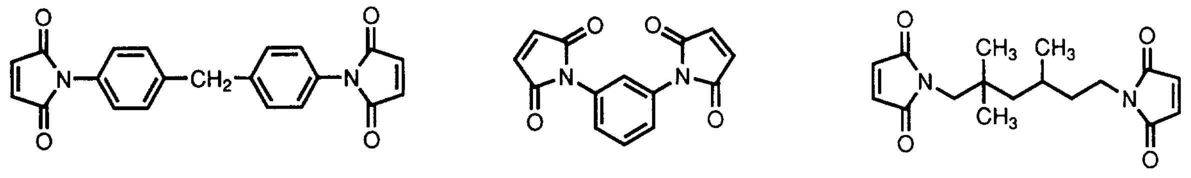
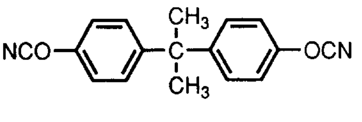


(55%) (30%) (15%)

Components of Compimide®353



Monomer structure of AroCy®B-30

2,2'-*bis*(3-allyl-4-cyanatophenyl)isopropylidene

2,2'-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene

Figure 1 Monomers and blends studied in this work

Ciba-Geigy Corporation), Louisville, KY and the BMI blend Compimide®353 (C-353, monomer blend represented in *Figure 1*) obtained from Shell-Technochemie, Dossenheim, Germany. The propenyl-functionalized monomer, 2,2'-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene (*Figure 1*), forms the basis of a British patent application[7]. In order to prepare 2,2'-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene the precursor, the propenyl-substituted *bis*-phenol was first obtained by isomerizing 2,2'-*bis*(3-allyl-4-hydroxyphenyl)isopropylidene using a standard preparative route[8].

2,2'-Bis(3-propenyl-4-hydroxyphenyl)isopropylidene. A 1 l, three-neck flask, fitted with a still-head and condenser for a downward distillation, was charged with 2,2'-*bis*(3-allyl-4-hydroxyphenyl)isopropylidene (50 g, 162 mmol) and a saturated solution (*ca.* 50% w/v) of potassium hydroxide in methanol (150 cm^3). The mixture was distilled slowly until the temperature of the solution reached 110°C. The still-head was removed, an air condenser put in its place, and the reaction mixture boiled gently under reflux for 7 h. The reaction mixture was cooled to room temperature, acidified with concentrated hydrochloric acid (20 cm^3) and extracted into dichloromethane (3 x 30 cm^3). The crude product was washed with deionized water and dried over anhydrous magnesium sulfate (24 h) before being concentrated on the rotary evaporator to yield a very viscous, amber oil with a distinctly pungent odour. ^{1}H n.m.r. analysis revealed that the product contained a mixture of geometric isomers (both *trans* and *cis* about the propenyl C=C double bond) in the approximate ratio 4 : 1. ^{1}H n.m.r. (300 MHz, D_6-acetone, ppm from TMS): 8.16 (s, Ar-$\underline{H}$, *trans*-isomer), 7.94 (s, Ar-O$\underline{H}$, *cis*-isomer), 7.27–6.70 (c.m., Ar-H), 6.70–6.64 (d of d, 2 x *trans*-C$\underline{H}$=CH–CH_3), 6.54–6.54 (d of d, 2 x *cis*-C$\underline{H}$=CH–CH_3), 6.21–6.14 (m, 2 x *trans*-CH=C$\underline{H}$–CH_3), 5.73–5.71 (m, 2 x *cis*-CH=C$\underline{H}$–CH_3), 1.83–1.81 (d of d, 2 x *trans*-CH=CH–C$\underline{H}_3$), 1.69–1.62 (d of d, 2 x *cis*-CH=CH–C$\underline{H}_3$), 1.61 (s, 2x^{i}Pr C$\underline{H}_3$).

2,2'-Bis(3-propenyl-4-cyanatophenyl)isopropylidene. To prepare 2,2'-*bis*(3-*trans*-propenyl-4-cyanatophenyl)-isopropylidene a three-neck, 500 cm^3 round bottom flask equipped with a dropping funnel, overhead stirrer, and thermometer was charged with the newly isomerized 2,2'-*bis*(3-propenyl-4-hydroxyphenyl)isopropylidene (47.3 g, 153.2 mmol), cyanogen bromide (45.09 g, 0.43 mol) and freshly distilled acetone (200 cm^3). The flask was cooled to −30°C and freshly distilled triethylamine (43.08 g, 0.43 mol) was added dropwise over 45 min to the vigorously-stirred mixture while the temperature was maintained at −25 to −30°C by immersion in a dewar flask containing an acetone/liquid nitrogen mixture. The reaction mixture was stirred for a further 90 min while warming to room temperature, and the product isolated by slowly decanting the solvent from the reaction mixture into ice water (1.5 l) whilst adding ice water (1 l) to the remaining precipitated salts. After repeated extraction into dichloromethane (9 x 50 cm^3) and concentration on the rotary evaporator, the crude product resembled a mobile amber liquid. The crude product was washed first with 5% NaOH solution and then deionized water. The cleaned product was again extracted into dichloromethane and dried over anhydrous magnesium sulfate, filtered and isolated on rotary evaporator to yield a straw coloured oil in good yield (*ca.* 40 g). Upon standing for approx. 1 week at room temperature, large white crystals had formed in the bottom of the flask containing the crude oil, and a portion of this crystalline product was dried (of the surplus oil—the other geometric isomer—coating it). ^{1}H n.m.r. analysis of the crystalline mass revealed that it consisted of a single isomer (while the mother liquor consisted of a mixture of isomers). The *trans*-isomer crystallizes as a waxy, white solid, while the *cis*-isomer remains a mobile, amber oil at room temperature. *FT* i.r. (KBr disk): 3063 (w), 2977 (s), 2936 (m), 2877 (w), 2272 (s), 2211 (s), 1640 (w), 1611 (w), 1594 (w), 1493 (vs), 1453 (m), 1203 (s), 1172 (vs), 1135 (vs), 965 (m), 820 (m) and 780 (m) cm^{-1}; ^{1}H-n.m.r. (300 MHz, D$_6$-acetone, ppm from TMS): 7.56–7.54 (2H, d, 2 × Ar-H), 7.47–7.44 (4H, d of d, 4 × Ar-H), 7.34–7.25 (4H, d of d, 4 × Ar-H), 6.59–6.53 (2H, d of d, 2 × *trans*-$\mathrm{C\underline{H}{=}CH{-}CH_3}$), 6.43–6.29 (2H, c.m., 2 × *trans*-$\mathrm{CH{=}C\underline{H}{-}CH_3}$), 1.96–1.87 (6H, d of d, 2 × *trans*-$\mathrm{CH{=}CH{-}C\underline{H}_3}$), 1.75 (6H, s, 2 × ^{i}Pr $\mathrm{C\underline{H}_3}$). Found: C 77.3%, H 6.1%, N 8.0%; calculated: C 77.1%, H 6.2%, N 7.6%.

Equipment

Infra-red spectra were recorded with a Perkin-Elmer 1750 Fourier transform i.r. spectrometer interfaced with a Perkin-Elmer 7300 computer; the samples were presented as either thin films or as KBr disks depending on the physical state of the material. The ^{1}H n.m.r. spectra were recorded at 298 K in D$_6$-acetone using a Bruker AC300 pulse Fourier transform nuclear magnetic resonance spectrometer operating at 300 MHz. The chemical shifts (δ) are given in parts per million (ppm) and are reported relative to the tetramethylsilane (TMS) internal standard. Melting points were determined using a Koffler hot-stage microscope. Differential scanning calorimetry (d.s.c.) was performed at a heating rate of 10 K min^{-1} under nitrogen (40 cm^3 min^{-1}) using a Du Pont 910 calorimeter interfaced with a Du Pont 9900 computer/thermal analyser. Monomer samples (10 ± 2 mg) were run in sealed, uncoated aluminium d.s.c. pans. 10-Ply composite samples (see below for preparation) for dynamic mechanical thermal analysis (d.m.t.a.) were prepared to the following dimensions (50 × 10 × 2 mm^3). Analysis of samples was carried out using a Polymer Laboratories (PL) analyser interfaced with a Compaq Diskpro 286 personal computer running PL software. The composite samples were oscillated in a dual cantilever flexural mode at a fixed frequency of 10 Hz while being scanned under nitrogen (40 cm^3 min^{-1}) at a heating rate of 4 K min^{-1}.

Preparation of cured carbon-fibre tow samples

Single tow samples (Courtaulds E-XAS fibre, 12 000 filaments) were impregnated through a bath containing the solvated monomers/prepolymers (in dichloromethane) and then through a die (1.5 mm in diameter) to remove the excess resin. The impregnated tow was cut and mounted on a frame to undergo cure in an air oven (1 h @ 170°C, 2 h @ 180°C). After being cut into test samples, the resin-impregnated tows were subjected to free standing post cure (1 h @ 220°C).

Preparation of carbon-fibre prepreg samples

Pre-impregnated carbon-fibre (prepreg) was prepared using a dip-winding technique. Composite lay up involved the preparation of 10-ply unidirectional laminates for the majority of the mechanical tests. In the case of double cantilever beam fracture toughness (G_{IC}) test specimens, 18 ply laminates were prepared (a 40 mm polytetrafluoroethylene film insert was placed between plies 9 and 10 in the lay-up sequence prior to cure to produce a laminate specimen containing a pre-initiated crack). All laminate samples were cured in an autoclave using the following cycle. After lay up vacuum was applied and held for approx. 10 h, or overnight. At the start of the schedule a pressure of 6 bar was applied, with the vacuum being vented as the pressure reached 2 bar. A heating rate of 2 K min^{-1} was used to bring the stack to a cure temperature of 180°C at which point it was held isothermally for 3 h to effect cure. After cure the stack was cooled at 3 K min^{-1} to 65°C and the cured laminate panel released from the bed plate. A free standing post cure (comprising a minimum of 1 h @ 220°C, but varying according to the resin system) was applied to all panels.

Initial test pieces were prepared either as homopolymers or as simple stoichiometric blends. These initial blends were used to establish a baseline for later testing in which composition was systematically varied to investigate the influence of individual components in the blend. Subsequently the influence of both the functionalized CE and the BMI : CE (total) ratio was also examined. The selection of a blend in which the BMI component is a major component reflects the lower cost of this component relative to the CE and the desire to produce a modifier for BMI resin systems.

Analysis of cured carbon-fibre composite samples

Density measurements. The density of both the cured neat resins and laminate samples was determined using a British standard (BS 2782 pt 6 method 620A) involving a displacement method. The fibre content of the cured laminate was based on a sulfuric acid/hydrogen peroxide digestion technique outlined by the Composite Research Advisory Group (CRAG)[9]. Ultrasound tests (C-scans) were carried out on the cured laminate samples in order to determine their void content. In all cases, only good laminates (with no detectable flaws and acceptable fibre content values 65 ± 10%) were used in subsequent mechanical tests.

Water absorption measurements. Water absorption tests were performed on six pre-weighed, single carbon-fibre tow samples (50 × 1.5 mm^2, fibre content 65 ± 5%) in a drying pistol. Tests were performed at 70% relative humidity (RH) at room temperature and at 75% RH at 70°C.

Interlaminar shear strength measurements. Interlaminar shear strength (ILSS) data were obtained using an Instron universal testing apparatus with a loading roller diameter of 10 mm and support rollers of 6 mm in diameter. The span between support rollers was accurately set to cover 10 mm. Five rectangular samples (each 20 × 10 × *ca.* 2 mm^3) were cut from a 10-ply unidirectional panel, that had previously been C-scanned, sectioned using a wet diamond saw and sanded using fine emery paper. The sample was carefully mounted in the frame, ensuring that it was exactly perpendicular to the roller axes. Compressive loading was initiated at a rate of 10 mm min^{-1} causing failure within 15–45 s.

Flexural strength measurements. Flexural tests were carried out on 5 rectangular 10-ply unidirectional laminate samples (120 × 10 × *ca.* 2 mm^3). The samples were mounted in an aligned test frame fitted with a loading roller of diameter 25 mm and two support rollers of diameter 10 mm (separated by an accurately set distance of 80 mm). Each specimen was loaded at a rate of 10 K min^{-1} by compression through the centre roller, causing failure in 30–120 s.

Compressive test measurements. Five Celanese-type specimens[9] were prepared from 10-ply unidirectional laminates (incorporating a 10 mm test section). Samples were mounted in a modified Celanese jig, ensuring that the sample was accurately aligned perpendicular to the test jig. The compressive load was increased at a constant rate of 1 mm min^{-1} (specimen failure occurred within 30–120 s).

Fracture toughness (G_{IC}) *measurements.* The double cantilever beam (DCB) test sample for G_{IC} fracture toughness measurements was prepared according to the CRAG procedure (dimensions 20 × 120 × 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. Readings of load and crack displacement 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, giving a total of 17 readings. Three methods of data reduction were applied, using in-house programs, the data quoted being those obtained by Corrected Beam Theory at peak load[10].

RESULTS AND DISCUSSION

Spectral data

The salient features of the *FT*i.r., and ^{1}H n.m.r. spectra are given in the Experimental section and their significance is discussed below. Of particular note is the disappearance of the signals at 994 cm^{-1} (m), 919 (m) cm^{-1} corresponding to the $-CH{=}CH_2$ moiety in the allyl compound to be replaced with the signal at 965 (m) cm^{-1} corresponding to the *trans* $-CH{=}CH-$ stretch. The propenyl spectrum also displays a more intense band at 2977 cm^{-1} (s) corresponding to the newly-appeared methyl group ($C-CH_3$ stretch) in the propenyl residue[11]. The appearance of an intense doublet at 2272 and 2211 cm^{-1} corresponding to the $C{\equiv}N$ stretch (and characteristic of compounds bearing the cyanato moiety)[11], and the disappearance of the intense, broad absorbance at *ca.* 3100–3700 cm^{-1} corresponding to the O–H stretch of the *bis*-phenols[11] are of greatest diagnostic use in this respect. The ^{1}H n.m.r. spectra data are presented as a composite plot (*Figure 2*). The propenyl-substituted dicyanate ester (*Figure 2*, trace a) displays a distinctly different spectrum from that of the allyl-substituted analogue (*Figure 2*, trace b). Chemical shifts attributed to the presence of olefinic protons and methyl protons in

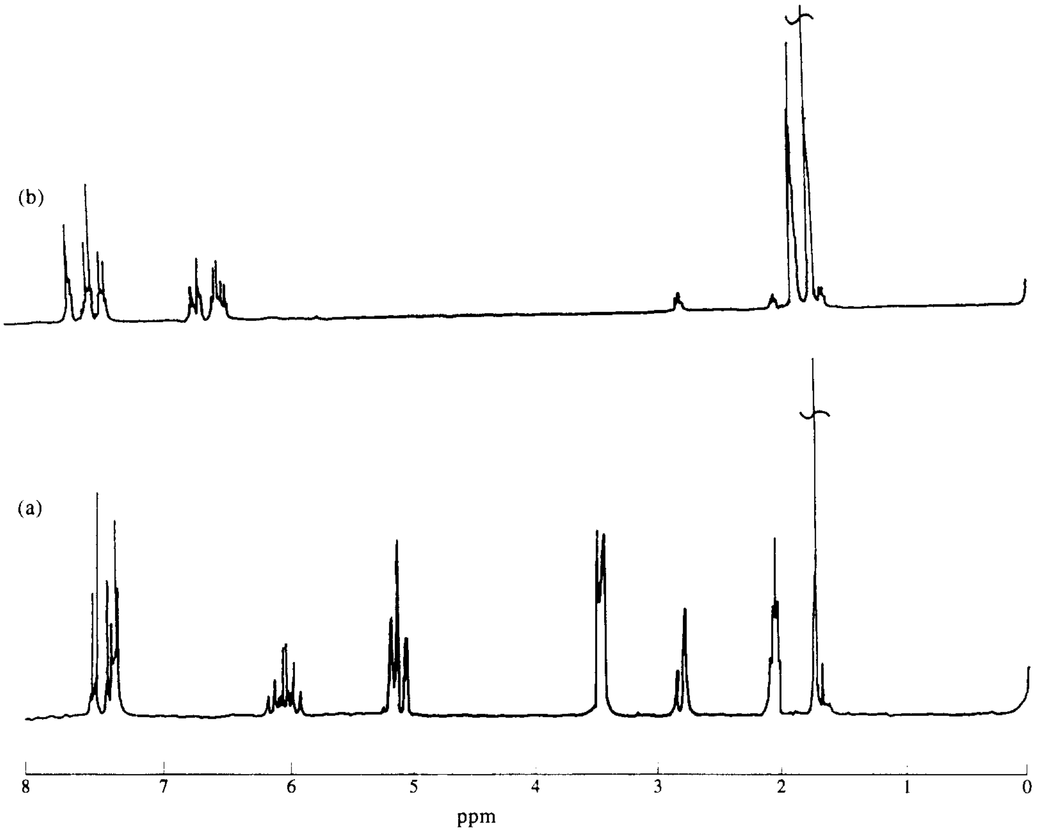


Figure 2 ^{1}H n.m.r. spectra (300 MHz, $[CD_3]_2CO$, 298 K, ppm from TMS) of 2,2′-*bis*(3-allyl-4-cyanatophenyl)isopropylidene (a) and 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene (b)

the propenyl group are clearly distinguishable from those of the allyl group.

D.s.c. data

A sample of the monomer 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene was analysed using d.s.c. to assess the thermal and catalysed curve (in order to provide information about the processing of the CE monomers). *Figure 3a* shows the effect of introducing the propenyl group into the CE monomer upon its reactivity (*Table 1*). Another functionalized CE monomer, 2,2′-*bis*(3-allyl-4-cyanatophenyl)isopropylidene, has already been reported[5a,b], and it was analysed under identical conditions, the results are shown in *Figure 3b*. The 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene displays a melt endotherm at 95°C and begins to undergo cyclotrimerization at *ca.* 110°C, the cure exotherm being complete by 200°C (*Figure 3a*). Further high temperature processes (which may include the homopolymerization of pendant propenyl groups) are also observed although the possibility of thermal degradation at this temperature should not be discounted.

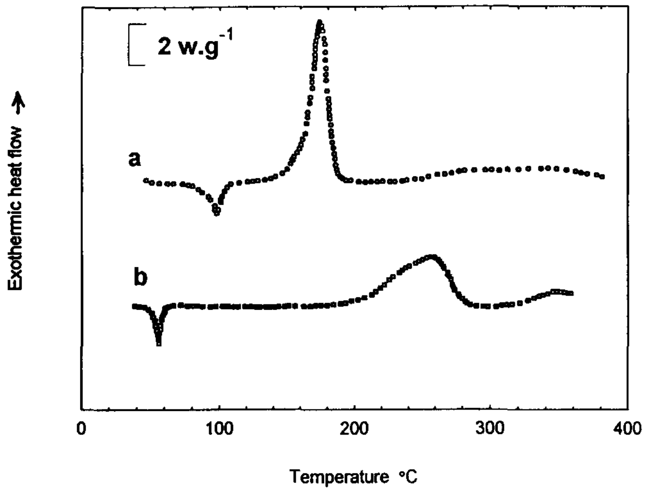


Figure 3 D.s.c. thermograms (10 K min^{-1}, under nitrogen) of 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene (a) and 2,2′-*bis*(3-allyl-4-cyanatophenyl)isopropylidene (b)

Table 1 Thermal characteristics of monomers, prepolymers and blends

Sample	T_m (°C)	T_{onset} (°C)	T_{max} (°C)	ΔH (J g^{-1})
A	—	186	262	173
B	77	254	317	226
C	—	133	259	220
D	45	150	257	614
E	95	110	167	584
			320	383
F	—	120	177	345
G	150	170	210	173
H	151	154	170	264

N.B. All d.s.c. measurements made at 10 K min^{-1} under nitrogen (40 cm^3 min^{-1})

A	Commercial Compimide® 353 bismaleimide blend
B	Commercial AroCy® B-30 cyanate ester prepolymer
C	Compimide® 353/AroCy® B-30 (1 : 1)
D	2,2′-*bis*(3-allyl-4-cyanatophenyl)isopropylidene
E	2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene
F	2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene/ Compimide® 353/AroCy® B-30 (1 : 1 : 1)
G	*bis*(4-maleimidophenyl)methane
H	2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene/ *bis*(4-maleimidophenyl)methane (1 : 1)
T_m	Crystalline melt endotherm
T_{onset}	Onset of polymerization exotherm
T_{max}	Exothermic peak maximum (or maxima)

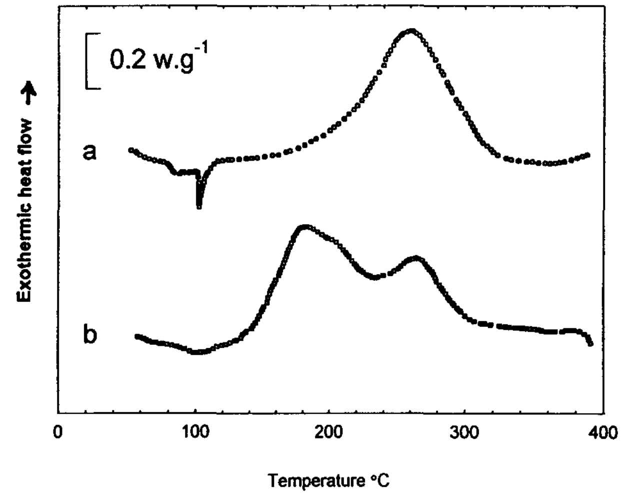


Figure 4 D.s.c. thermograms (10 K min^{-1}, under nitrogen) of blends of C-353/B-30 (1 : 1) (a) and C-353/B-30/2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene (1 : 1 : 1) (b)

Figure 4a illustrates the thermal behaviour of a 1 : 1 blend of B-30 and C-353. It should be noted that in this case whilst each component may undergo homopolymerization the resulting product should form an interpenetrating polymer network (IPN)[6] rather than a linked interpenetrating network (LIPN) discussed in earlier publications[5] arising from additional co-reaction of the propenyl-functionalized CE with the other two commercial components. The three-component (1 : 1 : 1) blend of 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene/B-30/C-353 was also analysed by d.s.c. (*Figure 4b*) and a bimodal exothermic peak is observed (spanning 121–310°C, with a peak maximum at 177°C and a high temperature shoulder at 275°C). This exothermic process presumably encompasses not only the homopolymerization of the BMI and CE components, but also the co-reaction of the propenyl-functionalized CE with the other two commercial components. Comparison of *Figures 4a* and *4b* indicates clearly which process is due to the Diels–Alder reaction (resulting from the propenyl-functionalized CE/BMI co-reaction at *ca.* 200°C) as this reaction is not possible in *Figure 4a*. Work is currently in progress to investigate the relative reactivity of *cis/trans* isomers (about the olefinic double bond) to the Diels–Alder co-reaction.

D.m.t.a. data

Composite samples were analysed by d.m.t.a. to assess the effect of the cure/postcure cycle on the glass transition temperature (T_g) of the polymeric network. For the purposes of this study, T_g was defined empirically as the temperature of the maximum value of the loss modulus (E''). The d.m.t.a. data are presented in *Tables 2–4* and as expected the BMI homopolymer shows the highest T_g (in excess of 300°C) while the commercial CE shows a T_g some 100°C lower (*Table 2*). While it is relatively easy to achieve a high T_g, it is important to combine such a value with a high fracture

Table 2 Mechanical data for 10-ply[a] unidirectional carbon-fibre laminates

	Equilibrium moisture content (%)		Log E''_{max} (°C)[b]						
Sample	70% RH at 25°C	75% RH at 70°C	1	2	ILSS (σ) (MPa)	f_F (σ) (GPa)	E_f (σ) (GPa)	F_{LC} (σ) (GPa)	G_{IC} (σ) ($J m^{-2}$)[a]
A	0.70	0.62	323		106.8 (5.0)	1.22 (0.12)	73.7 (4.0)	1.50 (0.05)	161.8 (11.8)
					110.5[c]	1.26[c]	76.3[c]	1.55[c]	176.4[c]
B	0.34	0.31	203		79.7 (4.5)	0.98 (0.13)	68.2 (4.1)	1.11 (0.07)	230.5 (16.9)
					84.6[c]	1.04[c]	72.4[c]	1.18[c]	285.8[c]
C	0.70	0.54	100	219	94.5 (5.1)	1.97 (0.13)	81.9 (3.1)	1.10 (0.04)	393.5 (8.7)
					114.5[c]	2.39[c]	99.2[c]	1.33[c]	479.4[c]
D	0.60	0.50	220	256	88.1 (5.2)	1.20 (0.14)	73.6 (3.2)	1.56 (0.05)	429.9 (16.2)
					105.4[c]	1.44[c]	88.1[c]	1.87[c]	526.6[c]
E	0.54	0.47	206	225	77.8 (5.0)	1.16 (0.13)	67.8 (3.2)	1.33 (0.04)	300.4 (15.1)
					86.9[c]	1.30[c]	75.7[c]	1.49[c]	363.5[c]
F	0.60	0.51	125	224	95.8 (4.6)	1.55 (0.07)	61.8 (3.3)	1.29 (0.04)	437.9 (8.1)
					100.9[c]	1.63[c]	65.1[c]	1.36[c]	534.2[c]
I	0.65	0.52	157	233	108.0 (4.5)	1.57 (0.11)	53.9 (2.5)	0.98 (0.06)	330.4 (11.0)
					106.4[c]	1.55[c]	53.1[c]	0.97[c]	455.4[c]

A Commercial Compimide® 353 bismaleimide blend
B Commercial AroCy® B-30 cyanate ester prepolymer
C Compimide® 353/AroCy® B-30 (1 : 1)
D 2,2′-*bis*(3-allyl-4-cyanatophenyl)isopropylidene
E 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene
F 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene/Compimide® 353/AroCy® B-30 (1 : 1 : 1)
I 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene/Compimide® 353 (1 : 1)

[a] Fracture toughness measurements performed on 16-ply laminates

[b] Dynamic mechanical measurements. Temperatures quoted in column 1 are the result of a post cure of 1 h at 220°C, while an entry under 2 indicates that the sample underwent post cure for 6 h at 200°C. All results for single tow samples, fibre content 65 ± 5%

[c] Data normalized for composite fibre content

Table 3 Mechanical data for 10-ply[a] unidirectional carbon-fibre laminates (BMI composition fixed at 50 wt %)

Sample composition	Log E''_{max} (°C)	ILSS (σ) (MPa)	f_F (σ) (GPa)	E_f (σ) (GPa)	F_{LC} (σ) (GPa)	G_{IC} (σ) ($J m^{-2}$)[a]
50 : 50 : 0	219	94.5 (5.1)	1.97 (0.13)	81.9 (3.1)	1.10 (0.04)	393.5 (8.7)
		114.5[b]	2.39[b]	99.2[b]	1.33[b]	479.4[b]
50 : 40 : 10	317	99.7 (5.0)	1.78 (0.08)	69.2 (2.7)	1.15 (0.03)	293.2 (12.0)
		109.7[b]	1.96[b]	76.1[b]	1.27[b]	350.4[b]
50 : 30 : 20	197	104.4 (4.5)	1.34 (0.07)	39.7 (3.2)	0.87 (0.05)	197.3 (9.6)
		123.0[b]	1.58[b]	46.8[b]	1.03[b]	227.6[b]
50 : 20 : 30	212	104.5 (5.2)	1.55 (0.09)	47.2 (2.9)	0.88 (0.03)	232.5 (8.4)
		125.6[b]	1.86[b]	56.7[b]	1.06[b]	281.7[b]
50 : 10 : 40	219	106.0 (4.9)	1.63 (0.15)	53.9 (3.3)	1.08 (0.03)	226.4 (10.1)
		110.1[b]	1.69[b]	56.0[b]	1.12[b]	249.0[b]
50 : 0 : 50	233	108.0 (4.5)	1.57 (0.11)	53.9 (2.5)	0.98 (0.06)	330.4 (11.0)
		106.4[b]	1.55[b]	53.1[b]	0.97[b]	455.4[b]

N.B. All samples composed of a blend of Compimide® 353/AroCy® B-30/2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene

[a] Fracture toughness measurements performed on 16-ply laminates

[b] Data normalized for composite fibre content

toughness value. The C-353/B-30 matrix (C) displays two distinct T_g values. This phenomenon has been observed[5a,b] before for polymer blends of unfunctionalized BMIs and CEs, and an earlier study[5b] presented ^{15}N n.m.r. data suggesting the formation of an IPN (rather than a true copolymer). The d.m.t.a. data (*Table 3*) suggest that in the case of the blends incorporating 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene/C-353/B-30 a T_g of greater than 300°C may be achieved with a blend containing 10 wt % of the functionalized CE monomer [i.e., C-353 : 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene : B-30 in the ratio 5 : 1 : 4, *Figure 5*]. A study of the ratio between total CE content and the BMI also revealed a single maximum value for T_g (386°C) with a

Table 4 Mechanical data for 10-ply[a] unidirectional carbon-fibre laminates (unfunctionalized : functionalized CE ratio fixed at 4 : 1)

Sample composition BMI : Total CE	Log E''_{max} (°C)[b]	ILSS (σ) (MPa)	f_F (σ) (GPa)	E_f (σ) (GPa)	F_{LC} (σ) (GPa)	G_{IC} (σ) ($J\,m^{-2}$)[a]
80 : 20	375	89.5 (4.5)	1.77 (0.11)	74.9 (3.3)	1.19 (0.04)	201.9 (10.1)
		102.5[g]	2.03[g]	85.8[g]	1.36[g]	242.3[g]
70 : 30	363	88.2 (5.3)	1.70 (0.16)	79.6 (3.4)	1.21 (0.03)	231.1 (9.9)
		103.4[g]	1.99[g]	93.2[g]	1.42[g]	292.0[g]
60 : 40	336	88.0 (5.3)	1.66 (0.11)	89.2 (3.2)	1.24 (0.02)	382.5 (9.6)
		108.1[g]	2.04[g]	109.6[g]	1.52[g]	497.3[g]
60 : 40	390[c]	—	—	—	—	281.4 (8.0)[d]
						363.9[g]
60 : 40	386[e]	—	—	—	—	265.3 (7.4)[f]
						338.3[g]
50 : 50	317	99.7 (5.0)	1.78 (0.08)	69.2 (2.7)	1.15 (0.03)	293.2 (12.0)
		109.7[g]	1.96[g]	76.1[g]	1.27[g]	479.4[g]

N.B. All samples composed of a blend of Compimide® 353/(AroCy® B-30/2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene)

[a] Fracture toughness measurements performed on 16-ply laminates
[b] All composite samples for DMTA postcured 6 h at 220°C unless otherwise stated
[c] Composite postcured 1 h at 220°C
[d] Composite postcured 6 h at 220°C
[e] Composite postcured 6 h at 220°C + 1 h at 250°C
[f] Composite postcured 1 h at 250°C
[g] Data normalized for fibre content

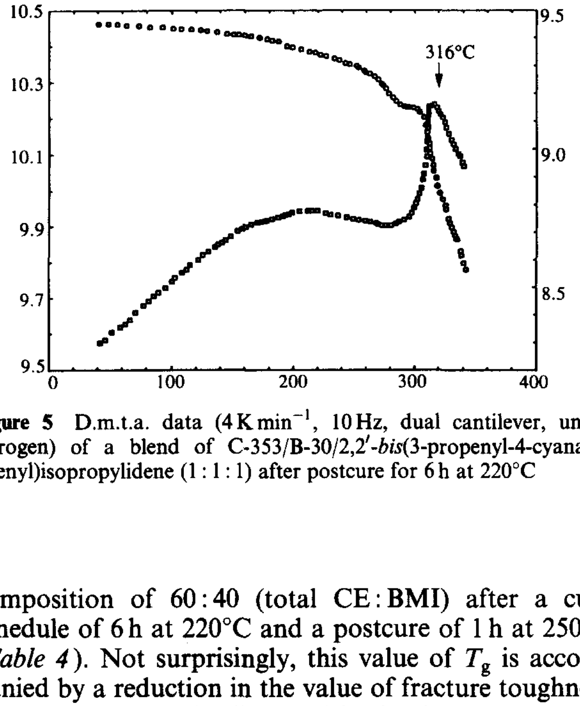


Figure 5 D.m.t.a. data (4 K min^{-1}, 10 Hz, dual cantilever, under nitrogen) of a blend of C-353/B-30/2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene (1 : 1 : 1) after postcure for 6 h at 220°C

composition of 60 : 40 (total CE : BMI) after a cure schedule of 6 h at 220°C and a postcure of 1 h at 250°C (*Table 4*). Not surprisingly, this value of T_g is accompanied by a reduction in the value of fracture toughness and this aspect will be discussed further below. However, the ability to achieve a high T_g value allows a compromise to be achieved with a moderately high T_g accompanied by an enhanced fracture toughness over the commercial homopolymers. T_g is a function of cure temperature and is invariably restricted to a maximum temperature not exceeding the postcure temperature +20°C due to diffusion control in the glassy polymer. The high T_gs observed in this work are due to continued cure above the initial T_g in the d.m.t.a. instrument (a kinetic effect) and as such are not the T_gs expected at the stated postcure cycle, likewise any fracture toughness properties would not correspond to these higher T_gs.

Water absorption

A series of test pieces consisting of short lengths of cured two samples were subjected to different treatments to determine the equilibrium water absorption characteristics. Samples were found to attain equilibrium very quickly (apparently within the first 24 h), with little significant increase noticeable thereafter, making calculated water absorption rates unreliable. Hence, equilibrium moisture absorption is reported (*Table 2*). In line with results reported by other workers[10] the BMI component displayed the greatest tendency for water absorption, with blends containing greater relative quantities of C-353 showing consistently higher equilibrium moisture content. The commercial CE prepolymer B-30 displays the lowest water uptake (always less than half that observed for C-353) while when cured as homopolymers, the novel alkenyl-functionalized CEs show intermediate water absorption values (cf. the commercial BMI and CE).

Blending these components produced the observation that the higher the BMI content of the blend, the greater the moisture uptake. However, when compared with homopolymer data, each blend absorbs considerably more water than expected by a simple rule of mixtures of the total BMI content. This is particularly true for the 50 : 50 blend of C-353 and B-30 (in which there is believed to be no co-reaction between the two components—analogous to the Mitsubishi Gas Chemical Corp. "Skyflex BT®resins"). It has been suggested[13] that the low moisture absorption reported for CE resins is attributed to the relatively open network structure that is formed (from linked *s*-triazine rings) on cure enabling a high rate of diffusion for absorption and egress of water. The BT-type resin is believed to form an IPN in which the two components are entangled, but not covalently bonded. In this fashion the BMI phase would effectively 'fill' the open structures in the network and hence lower the rate of moisture desorption. In the blends employing

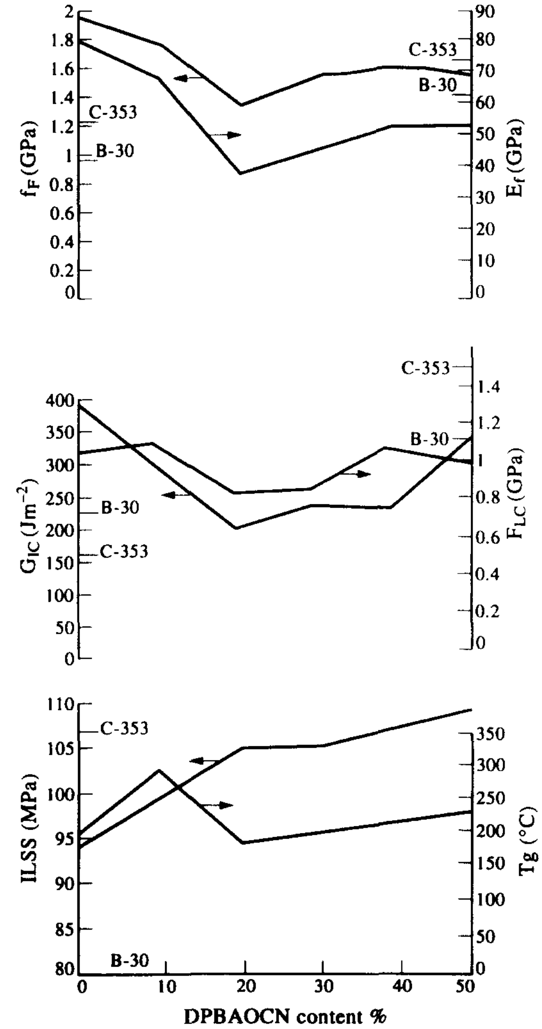


Figure 6 Combined mechanical data for 10-ply unidirectional carbon fibre reinforced laminates (Courtaulds E-XAS fibre, 12 000 filaments) for a blend of C-353, B-30 and 2,2′-*bis*(3-propenyl-4-cyanatophenyl)-isopropylidene (as a function of 2,2′-*bis*(3-propenyl-4-cyanatophenyl)-isopropylidene content, the C-353 content was held at a fixed value of 50%). Note G_{IC} measurements were made on 16-ply laminates

the alkenyl-functionalized modifiers improvements in moisture absorption are observed (cf. the BMI homopolymer and the C-353/B-30 blend).

Interlaminar shear strength measurements

In this study the greatest interlaminar shear strength (ILSS) values were obtained for composite samples incorporating the homopolymers of the propenyl-functionalized bisphenol A dicyanate ester (108.0 MPa) and C-353 (106.8) (*Table 2*). In general ILSS data for composite samples displayed a reduction in ILSS as the functionalized CE content was decreased (from 108.0 MPa with 50% 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene to 94.5 MPa with 0% 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene) (*Table 3*, *Figure 6*). Little variation was observed in ILSS with respect to the ratio of BMI : total CE content (*Table 4*) although in each case the ILSS data were lower than that obtained for composite samples prepared without functionalized CE monomers.

Flexural strength measurements

Flexural strength (f_F) and modulus (E_f) data for composite samples containing simple stoichiometric blends are displayed in *Table 2* (again Compimide 353 and AroCy B-30 are used for reference purposes). The greatest values recorded in this table are for a C-353/B-30 IPN ($f_F = 1.97$ GPa and $E_f = 81.9$). *Table 3* displays data for samples containing a fixed BMI content (of 50 wt%). Both flexural strength and modulus are seen to increase almost equally as the unfunctionalized CE content is decreased (with a discontinuity observed for blends containing 20 and 30% propenyl-functionalized CE, *Figure 6*). All BMI/CE blends show an improvement in flexural strength and to a lesser extent flexural modulus over the reference homopolymers (*Table 2*). As the Compimide 353 is blended with unfunctionalized CE both flexural strength and modulus increase, while incorporation of propenyl-functionalized CE leads to an increase in flexural strength, but a reduction in flexural modulus. Again as the total CE ratio was varied (while maintaining a BMI content of 50%), very little variation in flexural strength is observed (*Table 4*) although flexural modulus and strength appear to vary inversely (*Figure 7*).

Compression test measurements

The relationship between functionalized CE and compressive strength (F_{LC}) is shown in *Tables 2–4* and a similar trend to that obtained for flexural strength is observed. A discontinuity is observed for a 50% B-30 composition (*Figure 7*) and only marginal increases in compressive strength as unfunctionalized CE content is increased (*Table 3*, *Figure 6*).

Fracture toughness (G_{IC}) measurements

Considering the composites containing homopolymers and simple stoichiometric blends (*Table 2*) it is apparent

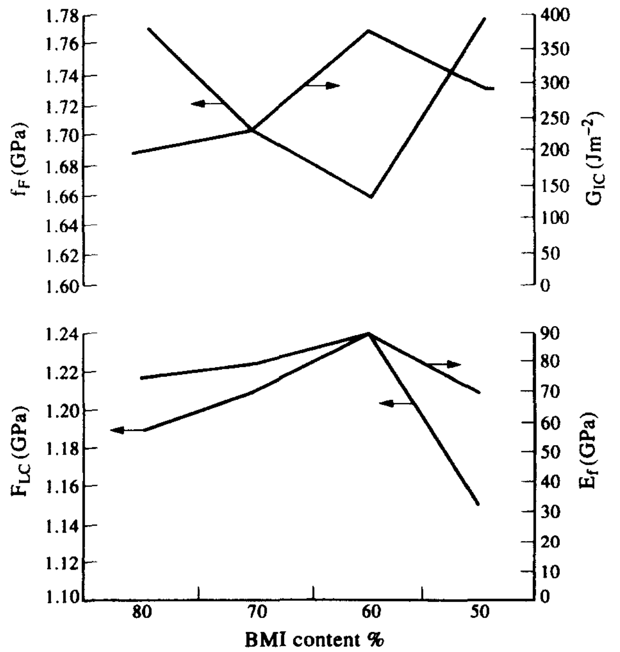


Figure 7 Combined mechanical data for 10-ply unidirectional carbon fibre reinforced laminates (Courtaulds E-XAS fibre, 12 000 filaments) for a blend of C-353, B-30 and 2,2′-*bis*(3-propenyl-4-cyanatophenyl)-isopropylidene (as a function of C-353 content, the ratio of B-30 : 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene was held at a fixed value of 4 : 1). Note G_{IC} measurements were made on 16-ply laminates

that the B-30 and C-353 homopolymers show poorer fracture toughness for crack propagation when compared with the alkenyl-functionalized CE monomers. In fact the 50 : 50 copolymer of the allyl-functionalized 2,2′-*bis*(3-allyl-4-cyanatophenyl)isopropylidene and C-353 displays a relatively high value of G_{IC} (429 J m^{-2}, *Table 2*). On blending, the improvement in fracture toughness is also significant. A simple blend of the commercial BMI and CE (which is believed to produce an interpenetrating network polymer in the same manner as a BT resin) increases the fracture toughness by nearly 150% over the single components alone (*Figure 8*). The incorporation of alkenyl-functionalized CE monomers (both allyl and propenyl) into a BMI and a BMI/unfunctionalized CE matrix produce a tertiary blend in which the functionalized CE may act as a bridging link for the other two components. Earlier work[5] has shown that reaction may occur between the allyl-functionalized CE and BMI *via* an 'ene'/Diels–Alder reaction. It is envisaged that the propenyl-functionalized monomer will react in a similar manner to commercial systems in which BMI monomers co-react with propenyl groups *via* direct Diels–Alder reactions[14]. However, it should be noted that the Diels–Alder co-reaction mechanism is more favourable than in the allyl-functionalized systems as in the latter the 'ene' reaction is the rate-limiting step. Simple three-component blends, in which components are blended equally, provide the highest values of fracture toughness observed in this work (*Table 2*, sample G, $G_{IC} = 438\,J\,m^{-2}$). *Figure 9* shows the relationship between the T_g of the three-component blends and fracture toughness (G_{IC}) (as a function of CE composition). It clearly illustrates the performance of the propenyl modifier in the three-component blend. A high T_g may be achieved with accompanying high fracture toughness for the composite specimens.

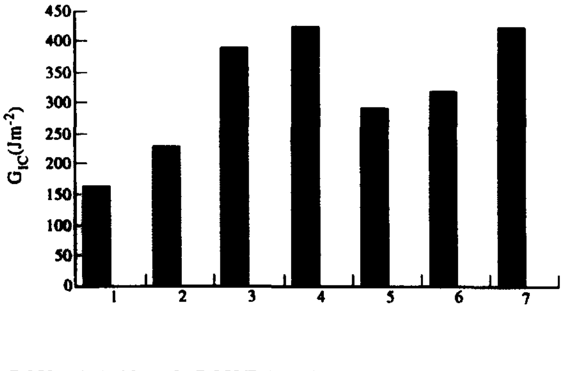


Figure 8 G_{IC} fracture toughness measurements of crack propagation in 16-ply unidirectional carbon fibre reinforced laminates (Courtaulds E-XAS fibre, 12 000 filaments) for a range of polymer matrices

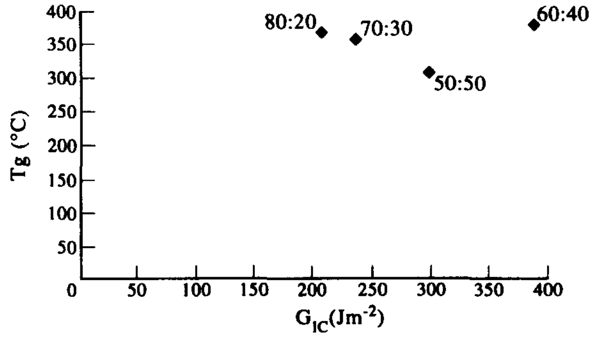


Figure 9 Plot of T_g vs G_{IC} fracture toughness (propagation) for blends of C-353, B-30 and 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene (as a function of BMI : total CE content)

CONCLUSIONS

The novel propenyl-substituted CE monomer, 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene, was prepared using reported literature methods. The cyanate ester product exists as two geometric isomers in distinctly different physical states. The *trans*-isomer crystallizes as a waxy, white solid, while the *cis*-isomer remains a mobile, amber oil at room temperature. This propenyl-substituted CE monomer, 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene, was analysed by d.s.c. and displays a melt endotherm at 95°C and begins to undergo cyclotrimerization at *ca.* 110°C, the cure exotherm being complete by 200°C.

D.m.t.a. data suggest that in the case of the blends incorporating 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene/C-353/B-30 a theoretical T_g of greater than 300°C may be achieved with a blend containing 10 wt % of the functionalized CE monomer (i.e., C-353 : 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene : B-30 in the ratio 5 : 1 : 4). A study of the ratio between total CE content and the BMI also revealed a single maximum value for T_g (386°C) with a composition of 60 : 40 (total CE : BMI) after a cure schedule of 6 h at 220°C and a postcure of 1 h at 250°C.

The commercial CE prepolymer B-30 displays the lowest water uptake (always less than one-half that observed for C-353). When cured as homopolymers the novel alkenyl-functionalized CEs show intermediate water absorption values (cf. the commercial BMI and CE). In blends employing the alkenyl-functionalized modifiers improvements in moisture absorption are observed when compared with the BMI homopolymer and the C-353/B-30 blend.

Interlaminar shear strength (ILSS) data for composite samples displayed a reduction in ILSS as the functionalized CE content was decreased. Little variation was observed in ILSS with respect to the ratio of BMI : total CE content (although in each case the ILSS data were lower than that obtained for composite samples prepared without functionalized CE monomers).

All BMI/CE blends show an increase in flexural strength and (to a lesser extent) flexural modulus over the reference homopolymers. Flexural strength and modulus are seen to increase almost equally when BMI is blended with unfunctionalized CE. However, when an alkenyl-functionalized CE is added to form a three component blend f_F while E_f is seen to decrease. The relationship between functionalized CE and compressive strength is similar to that obtained for flexural strength—only marginal increases in compressive strength are seen as unfunctionalized CE content is increased.

When incorporated into a blend both BMI and CE show significant improvements in fracture toughness over their respective homopolymers, an effect possibly due to morphological changes within the IPN resin matrix reducing the previously high crosslink density in the homopolymer matrices. This improvement in fracture toughness does however appear to be at the expense of the previously high T_g. If a functionalized aromatic cyanate is added as a third blend component the fracture toughness of the composite is significantly improved over the homopolymer, but with a lesser penalty in terms of T_g. The allyl-functionalized cyanate gave maximum fracture toughness when blended in high proportion ($G_{IC} = 300.4\,\mathrm{J\,m^{-2}}$, $T_g = 225°\mathrm{C}$) for a C-353 : B-30 : 2,2′-*bis*(3-propenyl-4-cyanatophenyl)isopropylidene blend (50 : 40 : 10). Functionalized CEs offer significant improvement in the high temperature/fracture properties of BMI : CE composites. In particular the propenyl-functionalized CE appears to offer such improvements at relatively low levels of incorporation. The latter observation may be explained by the potentially greater reactivity of the propenyl-functionalized CE over its allyl-functionalized analogue.

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