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Studying water uptake effects in resins based on cyanate ester/bismaleimide blends☆

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Abstract

The analysis of cured resin blends comprising cyanate ester and bismaleimide (BMI) to determine the chemical effects of long-term exposure to water is reported. The cured resin blends underwent accelerated water uptake by immersion in water at temperatures of up to 70°C, for a period of 18 months. Blistering and severe micro-cracking occurred, leading to severe weakening of the worst affected blends. Photomicrographs confirmed that the worst affected resins, containing high BMI contents, displayed two-phase morphologies. Thermogravimetric analysis and dynamic mechanical thermal analysis were performed on neat resin samples before and after immersion. Spectroscopy (near infrared Raman, diffuse reflectance and mid-infrared) was performed on powdered resin samples to determine the nature of the chemical changes occurring during the degradation. The elemental composition of the samples was also determined before and after conditioning. Crown copyright © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Water damage; Cyanate ester; Bismaleimide

1. Introduction

Advanced composite materials consist of reinforcing fibres (such as carbon) embedded within a matrix (such as an epoxy resin). The combination of these elements produces materials that have very high strength to weight ratios and, for this reason, they are used in applications where low weight and high strength are important (e.g. racing car monocoques and high-speed aircraft). For higher performance aircraft applications, where surface operating temperatures (particularly the leading edges) can reach 120°C at speeds exceeding Mach2 (and at altitudes of 40 000 ft) [1], conventional epoxy resins no longer offer adequate hot/wet performance and high performance matrix resins are required to withstand these temperatures. Consequently, high functionality epoxies, cyanate esters, polyimides and bismaleimides are examples of so-called “high performance” matrix resins [2].

Bismaleimides (BMIs) are probably the most important class of addition polyimides currently in use for advanced material applications, due to their high performance-to-cost ratio. However, in common with other addition polyimides, unmodified BMIs suffer from brittleness due to their high crosslink densities. Several approaches have been developed to increase the impact resistance, fatigue resistance and fracture toughness of the cured BMI resins [3]. One approach involves the incorporation of a flexible extended chain into the backbone of the BMI structure to increase the freedom of thermal expansion (due to the increased degree of freedom) and the tensile elongation (due to the reduced crosslink density), while maintaining processability. This approach has been commercially successful in producing a number of high molecular weight, linear BMI-terminated oligomers, via the Michael addition of BMIs and diamines, of which arguably the ‘Kerimid’ [4] and ‘Compimide’ [5] series are the most well known. Another approach has involved blending BMIs with other, inherently more tough, thermoplastic polymers such as polyetherimide [6] or co-reactive allylphenyl-, propenylphenyl- or allylphenoxy-terminated toughening agents [7,8].

The use of cyanate ester (CE)-BMI blends has already been the subject of extensive research and has found some commercial success. Indeed, some of the latest high performance, commercial systems are blends of cyanate, BMI and other resins (such as epoxy). However, unlike, for example, CE/epoxy networks [9], the ‘co-reaction’ between CE and maleimide functional

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Table 1
Compositions of the blends studied in this work

Blend designation	DCBA (wt%)	BMI (wt%)
1	100	0
2	90	10
3	80	20
4	65	35
5	50	50
6	35	65

groups is not well described in the literature, although the commercial ‘Skylex’ resins produced by Mitsubishi Gas and Chemical Corp. are an example of this concept [10]. Skylex resins comprise a blend of a BMI component and the dicyanate of bisphenol A (DCBA) in the form of a bismaleimide-triazine (BT) resin. It is believed that the ensuing polymer formed is an interpenetrating network (IPN), rather than a copolymer [11], but this may be dependent on the use of a cyanate-selective catalyst which causes the cyanate to polymerise before the BMI component [12]. In any case, depending on the composition of the blend (generally from 10–60 wt% BMI), a variety of materials may be produced e.g. with melting points ranging from 70 to 110°C and T_g values of the order of 230–290°C. Moisture absorption for the cured Skylex resins is quoted at between 1 and 3 wt% after saturation at 100°C [13]. It is well known that the presence of absorbed water can have a devastating effect on the thermomechanical properties of a resin. In the case of epoxy resins, this amounts, approximately, to a decrease in glass transition temperature, T_g, of 20°C per 1% water absorbed [14,15], so water uptake characteristics (and T_g values) are of great interest for high performance applications such as aircraft primary structures. As a consequence, a thorough knowledge of the possible effects on CE/BMI blends of exposure to moisture at elevated temperatures is key to the future use of these materials in these applications. This paper aims to determine the chemical nature of the changes in a ‘BT’ type resin, caused by water exposure, that has lead to visible physical damage to the aged, cured resins.

2. Experimental

2.1. Starting materials

The resin blends comprised two commercially available materials: one, a low-molecular weight (30% reacted) prepolymer of bisphenol A dicyanate, DCBA; the other a low-melting point blend of three bismaleimide 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 sample blends were catalysed with copper(II) naphthenate (300 ppm Cu^{2+} by weight) and four parts *per* hundred parts resin (phr) nonylphenol. The prepolymers were first melt blended at approximately 80°C then the catalyst added. The resin mixture was then vacuum degassed at 80°C for approximately 15 min. Table 1 outlines the composition of the blends studied.

2.2. Curing of blends

A vertical steel mould ($250 \times 200 \times 2$ mm^3), coated with a silicone release agent, was pre-heated in a circulating air oven to 100°C. The resin was poured into the mould, and maintained at 100°C to allow it to fill the mould properly. The oven temperature was raised to 130°C (and held at this temperature for 30 min), the temperature was then raised to 170°C for a further 2 h, then allowed to cool to room temperature before the resin plaque was removed from the mould. The resin plaques underwent a free-standing post-cure in a circulating air oven for 4 h at either 220 or 250°C. These newly cured resins are denoted ‘virgin’ samples to differentiate them from the same material after conditioning (‘aged’ samples). In this work, where differentiation is required the following convention is adopted: (1v = ‘virgin’, 100% DCBA; 1a = ‘aged’, 100% DCBA).

2.3. Conditioning of blends

Long-term water uptake studies were performed at three different temperatures (20, 50 and 70°C). Polymer samples (approximately $20 \times 10 \times 2$ mm^3) were post-cured at 250°C and dried to constant weight in a vacuum oven at 100°C. They were then immersed in water and stored at the appropriate temperature for the duration of the study. For weighing, samples were removed and their surfaces dried. The length of immersion time was recorded at the time of weighing: weights were recorded after 1, 2, 4 and 8 h, then at intervals increasing roughly with the square of time.

2.4. Measurements

Thermogravimetric analysis (TGA) was carried out using a Perkin–Elmer TGA-7 thermal analyser. Finely powdered samples (2 ± 2 mg) were analysed in a platinum sample holder. Samples were heated from 50 to 900°C at 20 K min^{-1} in a nitrogen atmosphere (40 cm^3 min^{-1}). Dynamic mechanical thermal analysis (DMTA) was performed at a heating rate of 4 K min^{-1} under nitrogen (40 cm^3 min^{-1}) using a Polymer Laboratories dynamic mechanical thermal analyser Mk 2 with a bending/shear head. Neat resin samples ($20 \times 10 \times 2$ mm^3) were tested in a single cantilever flexural mode (with a free length of 5 mm) at a fixed frequency of 10 Hz between 30 and 300°C. Near infrared (NIR) Raman spectroscopy was

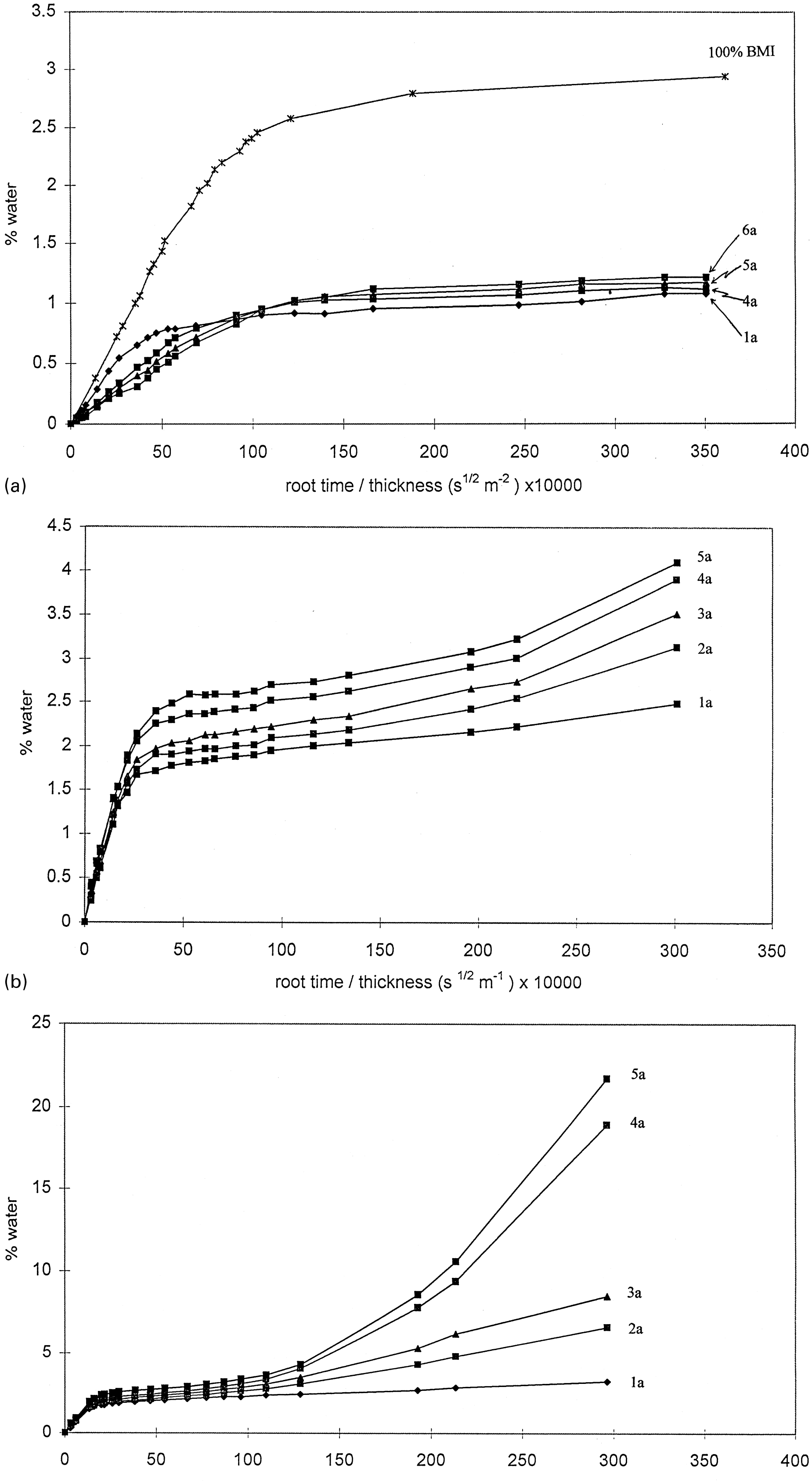


Fig. 1. Water uptake profiles of cured resin blends plotted as percent water uptake versus [(square root of time/thickness)] during conditioning at: (a) 20; (b) 50; and (c) 70°C.

carried out on neat resin sample plaques using a Perkin–Elmer 2000 NIR Raman spectrometer, with laser excitation from a Nd:YAG laser at 1.064 μm. Laser power was 850 mW and 16 co-added spectra were obtained at a resolution of 4 cm^{-1}. The same instrument, with beam-splitter and detector changes, was used to perform both diffuse reflectance spectroscopy (over the range 2800–10 000 cm^{-1}) and mid-IR spectroscopy (400–4000 cm^{-1}) on powdered resin samples in a sample holder/cup. Again, 16 co-added spectra were obtained at a resolution of 4 cm^{-1}. Elemental analysis was performed using a CE-440 elemental analyser.

3. Results and discussion

3.1. Moisture absorption of the resin blends

The water uptake profiles of the cured resin blends (plotted as percent water uptake versus [square root of time/thickness]) are presented in Fig. 1. Data are presented for samples conditioned at water bath temperatures of 20, 50 and 70°C. Initially, after immersion at room temperature, all the resins follow a similar pattern i.e. show Fickean type behaviour, with water uptake initially increasing with the square root of time, and eventually reaching a plateau at equilibrium water uptake of ca. 1% (Fig. 1a). Polycyanurates are noted for their low water uptake characteristics [11] and their hydrophobicity (believed to be due to the low polarity of the *s*-triazine ring) is retained even in the blends where BMI is present.

At 50°C, the water uptake profile is slightly different (Fig. 1b). In the first instance, the initial plateau values are higher, ranging from 1.8 to 2.5 wt%; in the second, water uptake begins to increase again, after the initial plateau has been reached. These features are more pronounced in samples containing higher BMI contents.

At 70°C, there is a very large variation in the profiles exhibited by the samples (Fig. 1c). Initially, the water uptake increased as before and appeared to reach a plateau at ca. 2–3 wt% (depending on blend composition). In all cases, the DCBA homopolymer displayed the lowest moisture uptake (ca. 2 wt%), and was the least affected, of the blends tested. However, after an extended period (e.g. 30–50 days), the samples containing BMI undergo a secondary increase in water absorption. Indeed, this feature became so marked that after a period of 400 days the blends displayed the following weight gains: 22 wt% (sample 5a); 18 (sample 4a); 8.5 (sample 3a); 6.5 (sample 2a). Furthermore, catastrophic damage was found to have occurred in the worst cases. After the same conditioning period, the DCBA homopolymer (sample 1a) displayed a weight gain of 3 wt%.

From the trend of the data, there appears to be a strong link between the BMI content of the blend and the moisture absorption that it displays. Those blends containing large quantities of BMI (particularly samples 4 and 5) display markedly higher values of moisture uptake than those containing either low (or no) amounts of BMI. The increase might initially be attributed to the presence of the BMI component, but these resin systems are not traditionally considered to be prone to high moisture gain. Unmodified BMIs may typically display comparable moisture uptake values to those obtained within this work. The diaminophenylindane-based BMI, RD85-101, (Ciba-Geigy) was reported as having displayed a moisture gain of 2.6 wt% after having undergone immersion in water for 48 h at 160°F (71°C) [16]. Similarly, moisture uptake of 4.30 wt% was reported for Compimide 796 [17] although, unfortunately no conditioning data were given in this reference. Toughened BMI systems, such as Matrimid 5292, may fare better with values of 1.4–1.5 wt% quoted [18] for samples exposed to 100% humidity for relatively short periods (2 weeks) at 38°C. Johncock and Tudgey [19,20] reported that the degree of water absorption in epoxies is probably related to a combination of the existence of polar groups in the network and the amount of free volume in the network. It is difficult to understand how the former might affect the present system since the concentrations of polar groups do not increase significantly on polymerisation, unlike epoxies. Moreover, they reasoned that the degree of frozen-in free volume is a function of T_g and this is an important factor in controlling the access of water to polar sites in the resin network.

3.2. Appearance of the virgin and aged samples

Before ageing, the virgin samples were generally transparent; the colour reflecting the BMI content (e.g. the DCBA sample 1, was a light amber, while the remaining samples, 2–5, were increasingly darker and red/brown). After ageing, the samples displayed varying levels of damage and brief descriptions are given below in Table 2 (photomicrograph of the actual samples are presented in Fig. 2).

Some of the resins (particularly samples 4a and 5a) displayed domains of different colour and appearance. In these cases, the damage was particularly acute with both blistering and severe micro-cracking occurring to the brittle outer layer of the sample. Interestingly, this was also accompanied by a marked difference in the physical state of the inner core, the latter becoming very soft and pliable; a possible indication of the presence of a high moisture content within this region (Table 3).

3.3. Infrared (IR) analysis

Both the virgin and aged samples were analysed as powders, using a sample holder/cup and a selection of representative spectra are presented in Fig. 3 (note bands have been normalised to an invariant signal due to aromatic ring breathing around 1000 cm^{-1}). Both virgin and aged samples display (mid-) IR spectra that are essentially similar. Although the spectra show interference from carbon dioxide (at 2360 cm^{-1}), the blends display peaks characteristic of

Table 2
Appearance of the samples after ageing (18 months immersed in water at 70°C)

Blend designation	Surface appearance/colour	Internal appearance
1a (100% DCBA)	Normal/red/brown	Transparent/no blistering evident
2a (90% DCBA)	Light yellow tinge	Transparent/no blistering evident
3a (80% DCBA)	Opaque/black/crazing	Inhomogeneity (brown specks) on one face
4a (65% DCBA)	Opaque/black/severe blistering and crazing	Caramel brown with white patches
5a (50% DCBA)	Opaque/black/severe blistering and crazing	Caramel brown containing large cracks and white patches

both the cyanate (vibrations due to C≡N stretch at 2217 and 2285 cm^{-1}) and bismaleimide (carbonyl C=O stretch at 1715, out-of-phase, and 1770 cm^{-1}, in-phase) components, while the DCBA homopolymer (1v/1a) does not contain the latter. The expected cyanurate/triazine (C=N stretch at 1557/1558 cm^{-1}) bands are somewhat lost in the aromatic bands. What is particularly interesting is that in the case of the virgin blends containing higher BMI contents (35 and 50%), the spectra apparently do not show bands representing the C≡N stretch. As the blends were carefully formulated to contain the components outlined in Table 1, this is particularly noteworthy. This observation suggests that at this spatial resolution (ca. 100 μm) the sample is displaying inhomogeneity. Fig. 3b shows the 50% blend, and the effects of the ageing process on both inner and outer surfaces. The changes are small, though show an enhanced carbonyl band for the aged inner sample.

3.4. Raman analysis

The Raman spectra of the virgin materials are shown superimposed in Fig. 4. The indistinct region occurring around 2200 cm^{-1} is due to self absorption of the Raman signal by water vapour in the instrument, a problem aggravated by the relatively high moisture content of the aged samples. The increasing concentration of BMI is manifest in the progression in C=O concentration, around ca. 1715 and 1776 cm^{-1}, an increasing band at 1387 cm^{-1}, the decreasing intensity at 704, 864, 989 (triazine ring), 1112 (triazine ring), 1175, 1218, 1559 cm^{-1}. Unfortunately, apart from 1a, which contains the DCBA homopolymer, the spectra of all the aged samples showed severe fluorescence interference, suggesting the presence of large chromophores and reducing the structural information, which could be derived from the spectra.

3.5. Near infrared (NIR) analysis

The NIR spectra of the virgin materials are shown superimposed in Fig. 5a. There are clear progressions in overtone and combination band intensities around 6096 (aromatic first overtone), 5245, 4876 and 4244 cm^{-1}. Although the signal from the NIR instrument was somewhat weak in the overlap region between the IR and NIR spectrometers, excellent agreement is found between the two. Both show differences between virgin and aged samples, and in particular there are significant differences between the inner core and outer coating of the aged sample containing 50/50 CE/BMI blend (5a). The latter is shown in Fig. 5b, with ageing samples showing lower 4570, 4877 and 6096 cm^{-1} bands.

3.6. TGA analysis

The virgin samples display no significant differences in thermal stability (Table 4) and, predictably, as the BMI content increases, this is accompanied by an increase in the thermal stability of the blend. In common with other published work [21], the DCBA hompolymer (1v) displayed two significant weight losses with maxima at ca. 460 and 600°C (both corresponding to weight losses of ca. 11–12% min^{-1}). Representative TGA weight loss profiles (for samples of 1v, 1a, 4v and 4a) are shown in Fig. 6. The study of the decomposition products of polycyanurates and appropriate model compounds [22,23] has led to the proposal of a thermal degradation mechanism which is initiated with hydrolytic cleavage of the ester linkage and is accompanied by subsequent decomposition of the triazine ring via both hetero- and homolytic decomposition reactions. The swelling and blistering of CE resin surfaces sometimes encountered at elevated temperatures is believed to be due to the evolution of carbon dioxide arising from the decarboxylation of carbamate species [24]. It is thought that the latter are formed when residual (sterically isolated) cyanate groups encounter airborne moisture at temperatures where the polymer undergoes significant segmental mobility (practically at temperatures in excess of 200°C). Pascault et al. [25] contend that the thermal decomposition of the dicarbamate of DCBA (to yield predominantly bisphenol A) occurs at relatively low temperatures ($150 < T < 200$°C) and also acts as a catalyst towards the polycyclotrimerization mechanism of the cyanate.

While there is little difference in the thermal stabilities of the virgin materials, a comparison of both virgin and their corresponding aged counterparts shows interesting differences (Table 4). It is particularly noticeable that the aged DCBA homopolymer (1a), whilst not unaffected, does not appear to exhibit such a marked reduction in thermal stability as the blends. Sample 1a still displays two major weight loss maxima (now present at slightly lower temperatures, ca. 440 and 560°C, with the first peak maximum corresponding to a rate of weight loss of ca. 12% min^{-1} and the second to ca. 10% min^{-1}). The presence of a weight loss at lower temperatures is observable (commencing at between 150 and 200°C) and possibly attributable to the evolution of gaseous moisture entrapped within the resin network.

While there is no systematic decrease in thermal stability, the samples containing higher BMI contents do display

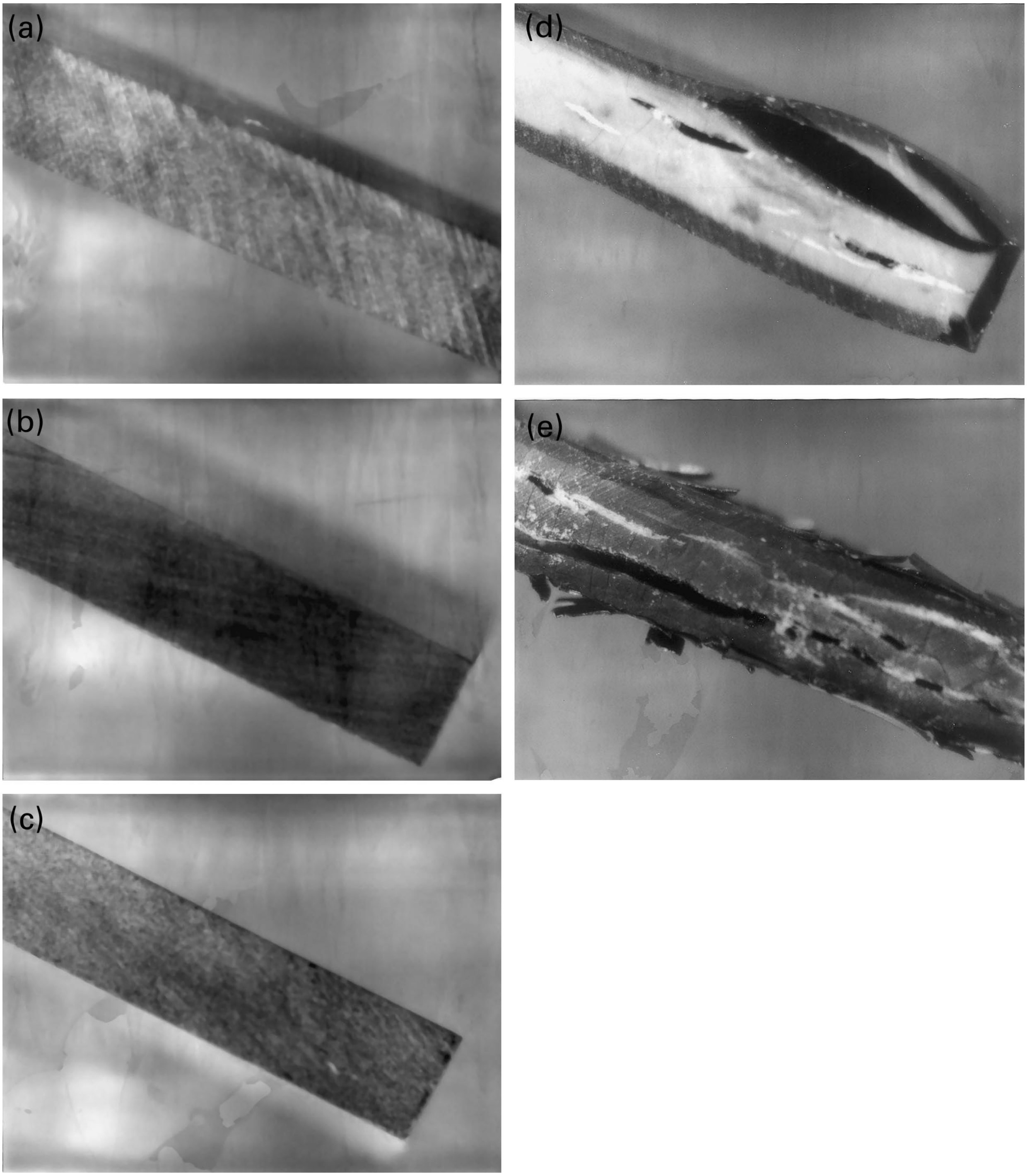


Fig. 2. Optical micrographs of aged samples after immersion in water (18 months at 70°C): (a) 1a; (b) 2a; (c) 3a; (d) 4a; and (e) 5a.

poorer thermal stability in the aged samples. For example, sample 4 displays very different TGA profiles before and after ageing has taken place. Sample 4v (Fig. 6) displays three main weight losses (ca. 450°C, ca. 13–14% min^{-1}; 580°C, ca. 8% min^{-1} and 640°C, ca. 9% min^{-1}). Whereas after ageing, the TGA trace of sample 4a reveals a different profile with weight losses at ca. 300°C, (ca. 4–5% min^{-1}), 440°C, (ca. 5% min^{-1}) and 560°C, (ca. 10–11% min^{-1}). It might be inferred that the BMI component is affecting the stability of the network. This would be a surprising conclusion since the thermal stability of polyBMIs is generally superior to that of polycyanurates. Stenzenberger et al. [26] observed that aromatic polyBMIs undergo a different thermal degradation to that of their aliphatic analogues. TGA-MS data show that the mechanism proceeds via cleavage of the succinimide ring, followed by carbon monoxide abstraction and the formation of a macroisocyanate. In general, the onset of thermal degradation of the aryl

Table 3
Microanalytical data for the virgin and aged blends (the calculated values are based nominally on the quoted empirical formulae of the monomers and stoichiometry of the blends, but do not take into account any additives/curatives)

Sample		% Carbon	% Hydrogen	% Nitrogen
	Calculated for $C_{17}H_{14}N_2O_2$	73.4	5.0	10.1
1				
Found for 1v		71.3	4.9	9.6
Found for 1a		70.5	4.7	9.3
2				
Found for 2v		71.1	4.9	9.3
Found for 2a		69.8	5.1	9.0
3				
Found for 3v		70.8	4.8	9.2
Found for 3a		67.6	5.2	8.4
4				
Found for 4v		69.5	4.9	8.7
Found for 4a		64.6	5.0	7.9
5				
Found for 5v		68.2	4.7	8.6
Found for 5a (outer)		62.4	4.8	6.9
Found for 5a (inner)		61.8	5.4	7.2

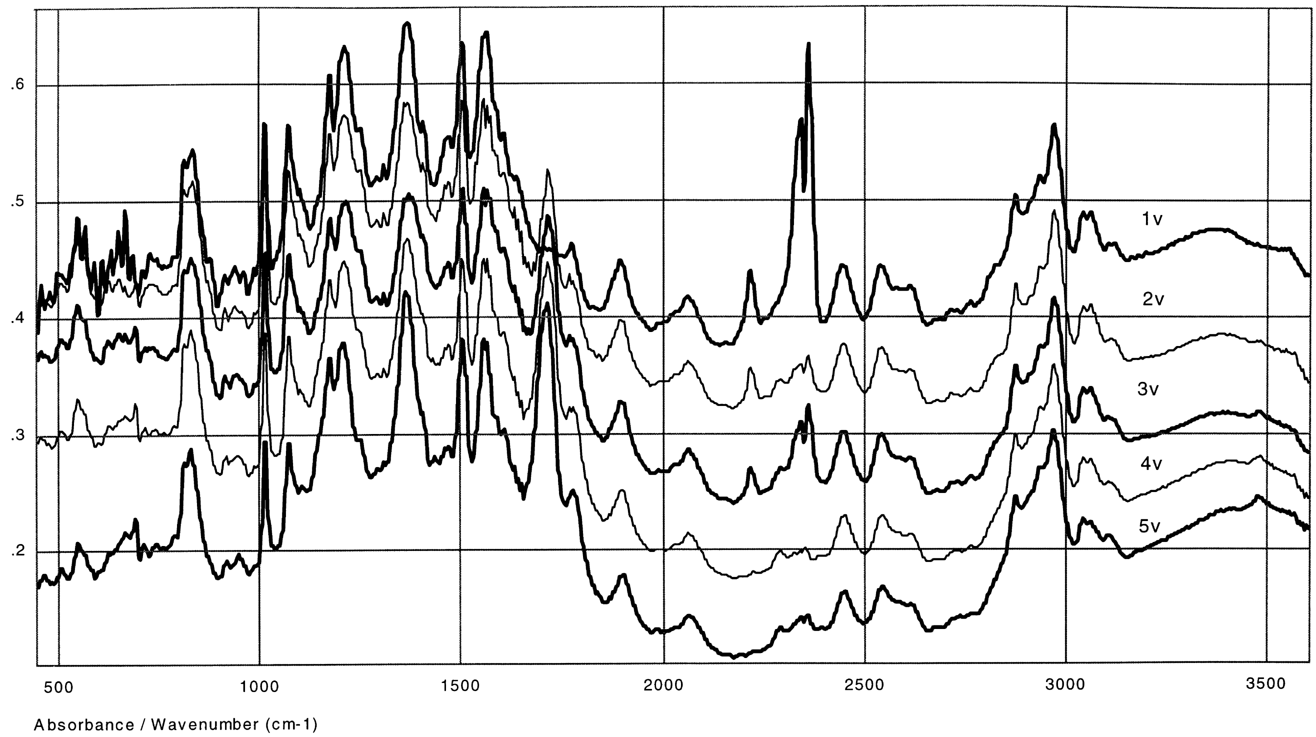
polyBMIs was observed to take place at temperatures in excess of 430°C (at a heating rate of $2\ \mathrm{K\ min}^{-1}$). Barton et al. [27] also reported similar findings for the thermal stability of bis-(4-maleimidophenyl)methane and bis-(4-maleimidophenyl)ether. It should be noted that the weight loss (5%) recorded at 365°C for the blend containing 35% BMI content (4v) might be related directly to the presence of absorbed moisture (see water absorption trace, Fig. 1). It has been noted that the blend containing the highest BMI content (5a) displayed a distinctly inhomogeneous, aged sample. An analysis of both ‘inner’ and ‘outer’ aged samples was attempted and, while the differences in thermal stability obtained were not significant, the weight loss profiles do differ.

3.7. DMTA analysis

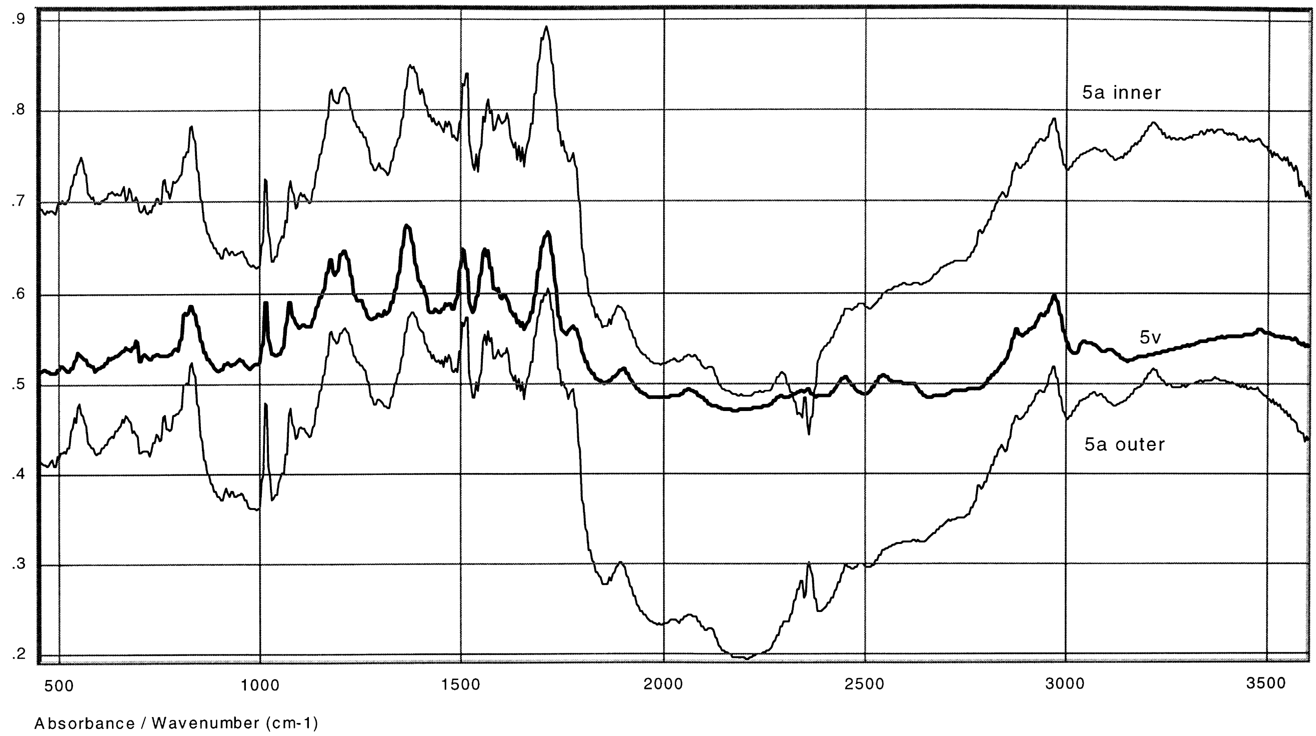
The DMTA for both virgin and aged samples are given below in Table 5 and representative traces are given in Fig. 7. While both $\log E''_{\max}$ and $\tan \delta_{\max}$ values are quoted in Table 5, the value of T_g that is quoted in the text refers to the former.

The DMTA traces for the virgin samples are similar in profile (although glass transition values vary slightly, according to the BMI content of the blend). Fig. 7 contains the DMTA data for sample 1v, the DCBA homopolymer. A relatively flat plot of E' precedes a sharp fall in modulus through the glass transition (from an initial level of $\log E' = 9.2$ Pa to a value of $\log E' = 7.2$ Pa at 300°C) followed by evidence of a rubbery modulus beyond this temperature. All samples show evidence of undergoing slippage in the DMTA clamps towards 350°C, but in the light of the preceding discussion of thermal degradation, measurements undertaken at these temperatures on the samples containing low BMI contents are largely academic as the data relate to a resin undergoing degradation. As the BMI content is increased, the DMTA traces appear to display a second, higher temperature transition. For example, sample 3v (Fig. 7) shows a relatively marked transition at ca. 245°C ($\log E'$ falls from 9.25 to 7.25 Pa at 300°C), attributed to the T_g of the polycyanurate, and the suggestion of a second, more diffuse, transition at ca. 360°C, the sample slippage makes a precise measurement impossible ($\log E'$ falls from 7.5 to ca. 6.5 Pa at 400°C). An earlier DMTA study of a ‘BT’-type resin [21] showed similar behaviour, albeit with more clearly defined transitions. These data, together with heteronuclear (^{15}N) NMR results confirmed the belief that the cured BT resin yields an IPN or a blend containing large domains of homopolymer, rather than a true copolymer, hence the presence of two discrete T_gs.

Unfortunately, attempts to analyse samples 4a and 5a met with little success as the brittleness of the samples caused them to disintegrate on even gentle handling, making a mechanical analysis practically impossible using this equipment. Where analysis was possible, after ageing there was a marked effect on the samples’ mechanical behaviour (Fig. 7). The DCBA homopolymer remained the least affected by the conditioning process, but even this sample appeared to display the effects of moisture plasticisation and damage arising from the moisture absorption/desorption (Fig. 7). The single T_g recorded for the virgin sample, 1v, was replaced by several apparent transitions in 1a: ranging from a small decrease in modulus at ca. 100–130°C, a larger transition at 150–175°C and the α-transition at 200°C. As the BMI content of the sample increased, the DMTA traces became progressively unsatisfactory: in the case of 3a (Fig. 7), the modulus begins to fall (from an initial level of $\log E' = 9$ Pa) after a scan



(a)



(b)

Fig. 3. (a) IR spectra of all virgin samples and (b) IR spectra of virgin, and aged samples of blend 5, showing the fundamental region between 450 and 4000 cm^{-1}. Spectra have been "normalised" to the alkane C–H stretching peak in this region. Balance of material is BMI.

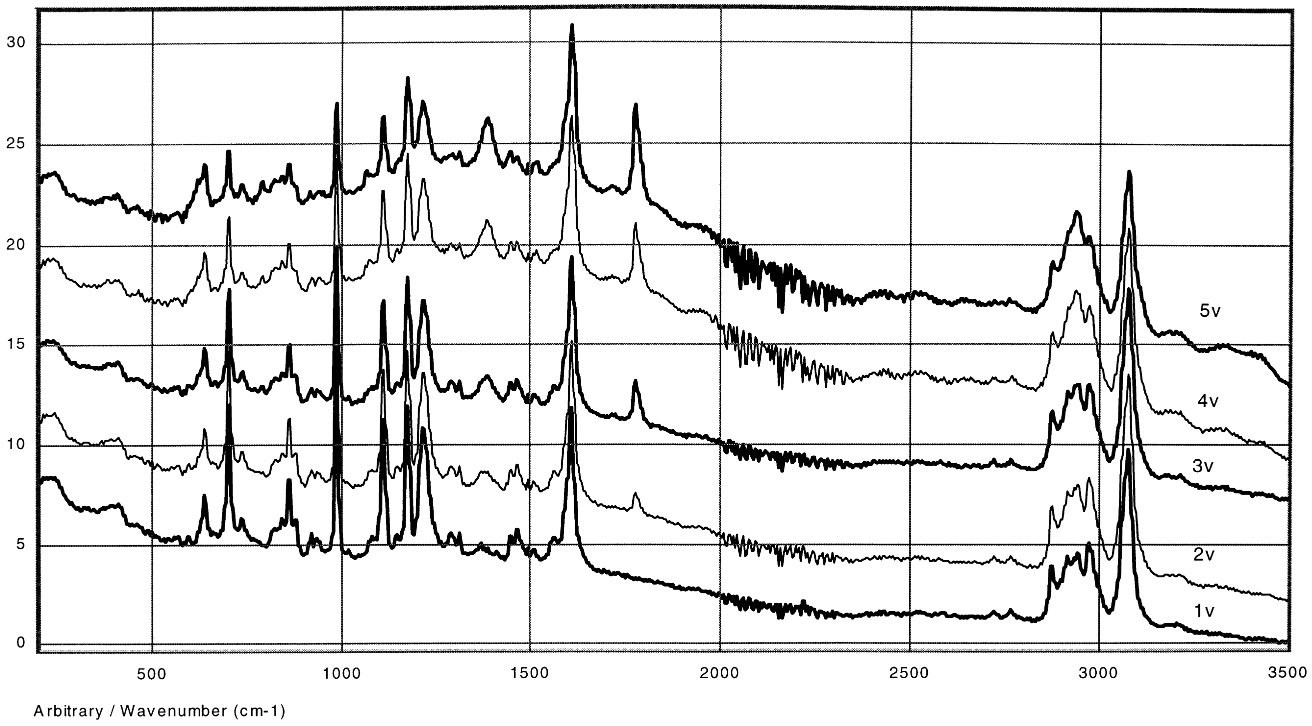


Fig. 4. Raman spectra (at 1.064 μm excitation wavelength) of virgin samples between 200 and 3500 cm^{-1}, normalised to the 1605 cm^{-1} band.

temperature of ca. 75°C and continues to drop steadily until the conclusion of the experiment at 250°C ($\log E' = 5.75$ Pa).

4. Conclusions

The cured resin blends of cyanate esters and bismaleimides underwent accelerated water uptake by immersion in water at temperatures of 20, 50 and 70°C, for a period of 18 months. After immersion at room temperature, the resins show Fickean type behaviour, with water uptake initially increasing as the square root of time, and eventually reaching equilibrium at ca. 1–1.5 wt%. At 50°C, the water uptake profile is slightly different as the initial plateau values are higher, ranging from 1.8 to 2.5 wt%; while the water uptake begins to increase again, after the initial plateau has been reached. These features are more pronounced in samples containing higher BMI contents. At 70°C, the water uptake initially increased normally and levelled out. However, after extended periods of time, the water uptake rate increased again and resulted, in the worst cases, in severe damage to the specimens. Blistering and severe micro-cracking occurred, leading to severe weakening of the worst affected blends. Photomicrographs confirmed that the worst affected resins, containing high BMI contents, displayed two-phase morphologies.

The reflectance method has been shown to be a powerful technique for obtaining vibrational data from these samples. The combination of techniques shows good agreement in assigning the molecular functionalities, and the changes with blend composition. It also suggests inhomogeneities at the 100 μm scale in even virgin materials. The use of Raman and near infrared may lend itself to remote, in situ measurements for monitoring the long-term quality and integrity of these advanced composite materials in service.

Work continues in the form of a longer-term ageing study of similar, and modified, CE/BMI blends in order to elucidate the nature of the degradation process.

Table 4
TGA data for virgin samples and their aged counterparts (20 K min^{-1} under nitrogen, 40 cm^3 min^{-1})

Sample	Temperature (°C) for given weight loss					
	5%	10%	20%	40%	60%	80%
1v	350	420	440	475	560	600
2v	310	375	425	465	555	628
3v	355	390	435	465	560	610
4v	370	410	449	510	575	635
5v	365	410	450	515	575	615
1a	270	330	390	440	500	575
2a	252	295	350	440	520	580
3a	215	265	325	440	547	595
4a	195	240	290	425	525	560
5a (inner)	185	245	285	440	535	570
5a (outer)	190	250	305	450	539	570

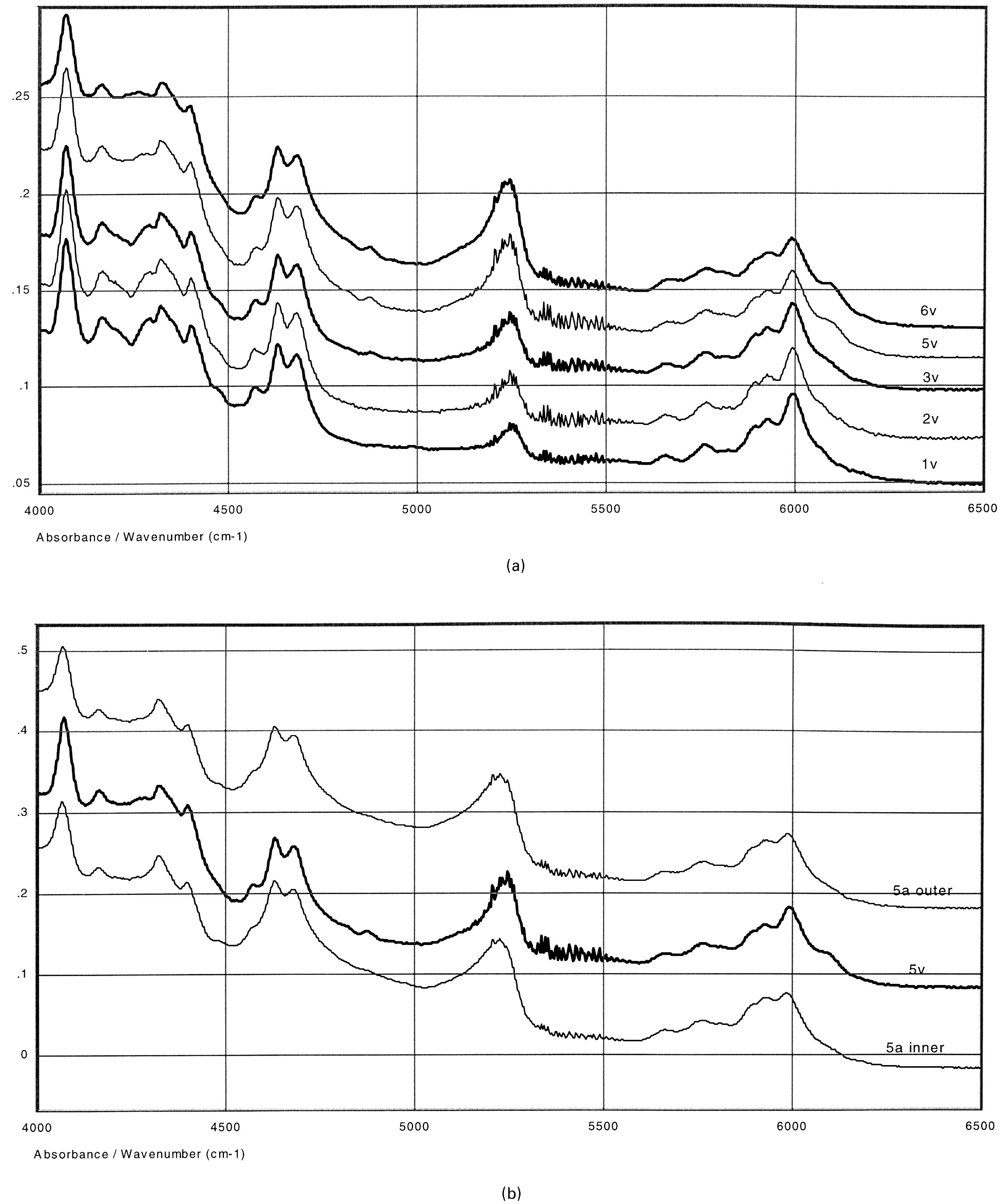


Fig. 5. (a) NIR spectra of all virgin samples showing the combination and overtone region between 4000 and 6500 cm^{-1}; (b) NIR spectra of virgin, and aged samples of blend 5, showing the fundamental region between 4000 and 6500 cm^{-1}. Spectra have been “normalised” to the alkane C–H stretching peak in this region.

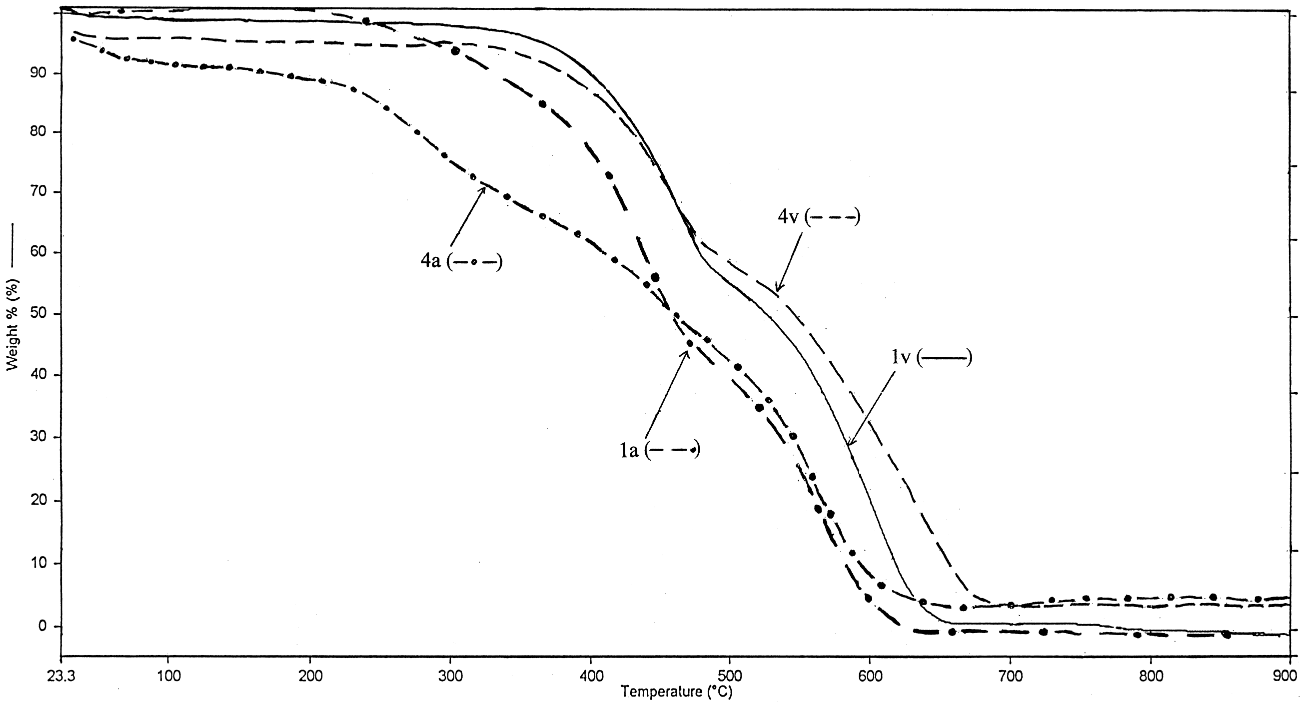


Fig. 6. TGA profiles of 1v and 1a, and 4v and 4a plotted as percent residual weight versus temperature.

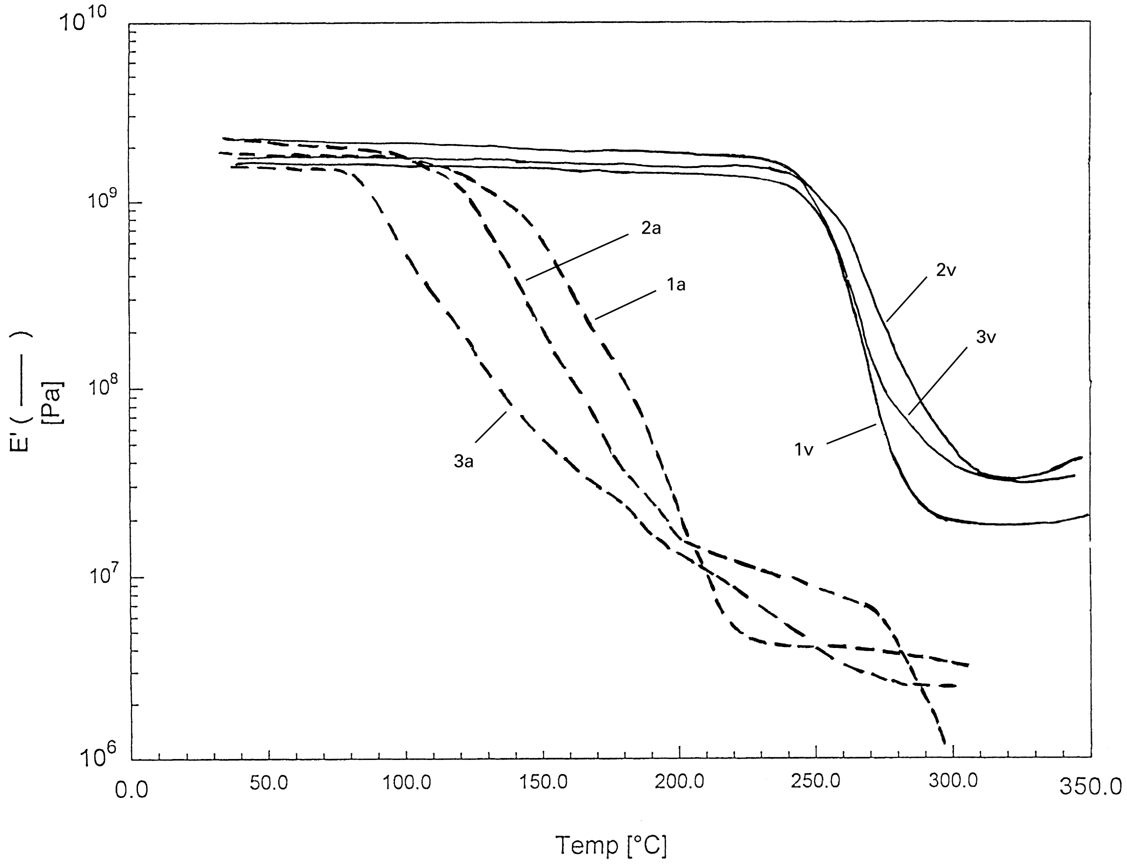


Fig. 7. DMTA traces for samples (a) 1v and 1a; (b) 2v and 2a; and (c) 3v and 3a (note virgin samples are denoted by a solid line, whereas the aged samples are denoted by a broken line).

Table 5
DMTA data for virgin samples and their aged counterparts (flexural mode 10 Hz, 4 K min^{-1} under nitrogen, 40 $\mathrm{cm}^3\,\mathrm{min}^{-1}$)

Sample	log E''_{max} (°C)	tan δ_{max} (°C)
1v	252	272
2v	250	272
3v	245	267
4v	237, 369	261
5v	221	244
1a	143	129, 168, 205
2a	118	150, 175, 200
3a	85	110, 145

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