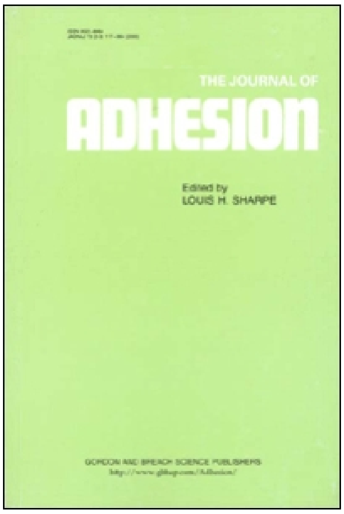

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A Study of the Interphase Region in Carbon Fibre/Epoxy Composites using Dynamic Mechanical Thermal Analysis*

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We have examined the effect of fibre addition on the glass transition temperature (T_g) of two epoxy resin systems (an amine cured and an anhydride cured epoxy system) using dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC). The presence of fibres changes the glass transition temperature (T_g) of an anhydride cured epoxy resin but does not affect that of an amine cured epoxy. The data suggest that two counteracting mechanisms are responsible for these changes: firstly, the presence of fibres causes a restriction of the molecular motion in the resin system, and secondly, the presence of carboxyl and keto-enol groups on the fibre surface inhibit curing of the resin close to the fibre, *i.e.* in the interphase region. The former increases the T_g and is a long range effect whereas the latter decreases the T_g and is a localised phenomenon. Changes in the dynamic properties of the interphase region are only detected when the samples are loaded in the longitudinal direction and not in the transverse direction where bulk matrix properties dominate. Sizing the fibres before their incorporation into the epoxy resin eliminates the variation in interfacial properties arising from differences in fibre surface chemistry.

KEY WORDS: Interphase; DMTA; carbon fibre/epoxy composites; plasma treatment; DSC; glass transition temperature.

INTRODUCTION

One of the main challenges to scientists studying interfacial phenomena in carbon fibre/epoxy composites is the ability to promote chemical bonding between fibre and resin. It is thought that chemical bonds exist between electrochemically treated fibres and epoxy resins; however, their concentration is too low to play a major role in fibre/resin adhesion[1]. Using a low-power air plasma significantly increases the surface concentration of chemical functionality. In this case, the presence of these chemical groups *has* been shown to play a major role in fibre/resin adhesion[2]. If chemical bonding is more prominent in composites made from air plasma treated fibres, then surely the "interphase" region in these materials will be affected.

The selective attraction of one of the resin components to the fibre surface will influence the localised curing of the resin and hence the glass transition temperature

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(T_g) of the interphase region. One method commonly used to measure T_g in both resin and composite samples is dynamic mechanical thermal analysis (DMTA).

While it is self-evident that different resin systems and curing cycles yield different glass transition temperatures, the mode of testing and the fibre orientation also play a significant role in the dynamic response of the material. Akay[8] pointed out that when testing unidirectional composites in flexure with the fibres oriented longitudinally, the fibres carry most of the load; therefore, changes due to the interface properties will be more easily detected, whereas in transverse loading the matrix properties dominate. In comparing DMTA results from both flexural and torsion testing modes, Dong[5] concluded that interfacial effects were highlighted more in the flexural mode.

The effect of fibre addition on epoxy composites has provided an extensive variety of DMTA results. A selection of transition temperatures reported in the literature is shown in Table I. Many research groups[5-7] have shown that the T_g of the composite is higher than that of the pure resin. Dong[5] suggested that the fibres reduce the effective

TABLE I
Summary of transition temperature results obtained by DMTA for commercially oxidised carbon fibre epoxy composites

Resin System	Fibre Type	Testing Method	Resin T_g(°C)	Composite T_g(°C)	Ref.
Ciba Geigy *LY 1927GB* Phenolic epoxy *Ciba Geigy* *HY 1927GB* Aliphatic polyamide	ENKA Tenax HTA300 Standard modulus V_f high	Dual cantilever	129	128	Harris[3]
DER 332 Dow Chemical DGEBA Fluka *diamino-diphenylmethane* *DDM*	Hercules AS4 *Low modulus* V_f high	Dual cantilever	188	185	Gerard[4]
Epon 828 DGEBA Methylene Dianiline	High Modulus XAS	Single cantilever	161	167	Dong[5]
EPIKOTE 828EL DGEBA Epikure 113	Courtaulds XAS Low modulus V_f 65%	Single cantilever	163	197	Thomson[6]
Epon 828 DGEBA *metaphenylene diamine* mPDA	Hercules AS Low modulus V_f 45–65%	Torsion	170	197	Ko[7]
Epon 828 DGEBA *metaphenylene diamine* mPDA	Hercules HMS High modulus V_f 45–65%	Torsion	170	219	Ko[7]

free volume and, therefore, increase the T_g of the resin. Others have shown that the T_g is lowered.[4,9,10] However, Harris *et al.*[3] found that the presence of carbon fibres have no effect on the T_g of an epoxy matrix. Garton[11] proposed that the nature of the resin system, *i.e.* whether it was cured with an amine or anhydride, determined whether the presence of treated fibres had any effect on the resin's glass transition temperature.

Gerard[4] and Peret *et al.*[9] both concluded that the decrease in transition temperature was due to the formation of a less cross-linked, more homogeneous epoxy network, due to the presence of oxidised[4] and T300[9] fibres.

Harries *et al.*[3] studied both longitudinal and trasversely oriented fibre samples and found that in both loading regimes the addition of fibres appeared to have little effect on the transition temperature. They concluded that neigher the resin cure reaction nor the resin network structure were affected by the presence of either an untreated or commercially oxidized fibre sufrace. Garton[12] used a combination of DMTA and DSC and detected differences in the measured T_g due to diffefences in fibre surface chemistry for an anhydride cured epoxy system. The differences in the transition temperature depended on the fibre treatment.

Many of the reasons for the observed increase in glass transition temperatures were attributed to preferential adsorption of one of the resin components at the fibre surface which creates an interphase region with a different composition from the bulk matrix. Ko,[7] using DMTA, concluded that it was the preferential adsorption of the epoxy oligimers onto the graphite basal planes which caused an increase in the T_g. This amine deficient region has a tighter network, lower average distance between cross-links and, therefore, a higher T_g. Since the epoxy oligimers are absorbed onto the graphite basal planes, the effect is more significant for fibres with a higher degree of crystallinity. After recording a decrease in T_g for T300 fibres,[9] Peret *et al.* then presented data from oxidised fibres (AS4) samples[13] showing an increase in the glass transition temperature. They proposed that this was due to the removal of the weakly-bound layers and increased functionality induced by oxidative treatment. This increased the fibre matrix bonding and decreased the molecular mobility within the interfacial zone. Further oxidation of the fibres to increase the surface functionality did not affect the transition any further.

There is also a wide variety of explanations for the results obtained from sized fibre samples. Harris *et al.*,[3] Chau,[14] and Gerard[4] could not distinguish between the presence of different sizes by DMTA, except in the case of an exceptionally thick size,[3] where the percentage of the sizing relative to the matrix was significant enough to cause a secondary peak associated with the T_g of the sizing resin. The presence of a secondary peak was also observed by Dibenedetto and Lex,[15] although they gave no indication as to thickness of the size. Both Garton *et al.*[11] and Peret *et al.*[9] have identified the presence of different sizing materials using DMTA. Garton *et al.*[11] showed that the presence of an epoxy prepolymer size on carbon fibres increases the T_g of the composite, since the sizing offers a resistance to molecular relaxation as it forms a more highly cross-linked network than that obtained with unsized fibres. Peret *et al.*[9] detected a decrease in T_g since the sizing material was deficient in catalyst and had a lower T_g than the bulk resin, therefore reducing the overall T_g of the composite.

In this paper, we report on a systematic series of results obtained from carbon fibre/epoxy composites using DMTA and DSC. We show the effects of altering the fibre surface chemistry and compare results from both anhydride and amine cured resin systems.

EXPERIMENTAL

Fibres

The fibres used for this study were Courtaulds XAU, XAS (commerically treated, unsized) and plasma-treated XAU fibres. The plasma treatment was performed in-house using a continuous treatment line, full details of which are given elsewhere.[2] In short, the fibres were exposed to an air plasma for 30 seconds.

Schematic representation of the fibre surfaces for sized and unsized fibres are shown in Figure 1. These representation have been derived from a thorough X-ray photoelectron spectroscopy investigation of these fibres.[16]

Resin System

Two different resin systems were used, an anhydride-cured epoxy system and an amine-cured epoxy system.

The Ciba Geigy difunctional epoxy MY750 was used in conjunction with nadic methyl *anhydride* (NMA) hardener and the catalyst K61B. The reaction mechanism is shown in Figure 2a. 100 g of MY750, 90 g NMA, and 4 g K61B were weighed out and stirred well; the mixture was placed in an oven at 60°C to lower the viscosity.

The Shell resin Epon 828 was used in conjunction with the *amine* hardener *meta*-phenylenediamine (mPDA). The reaction mechanism is shown in Figure 2b. 14.5 g of mPDA and 15 g of Epon 828 were weighed separately and heated at 60°C until the hardener had melted, they were then mixed with 85 g of Epon 828 and degassed before use.

Sample Preparation

Composite bars were made up using the "leaky mould" technique. The number of tows of fibres for the required volume fraction were wound around a metal frame and secured at each end; the fibres were then removed from the frame. Fibres that were to be sized were immersed in a butanone solution which contained 3% by weight of the tetra-functional epoxy MY720, removed and left to dry before further use. The tows of fibres were placed into the resin mixture and put back in the oven along with the mould for 10–15 minutes until the mould was hot. The fibre tows were stretched across the mould and clamped down. Each end of the tow was cut so that it was easier to remove from the mould after curing. The anhydride resin samples were cured for 2 hours at 120°C followed by a post cure at 180°C for at least 15 hours to ensure a fully cross-linked structure. Likewise, the amine system samples were cured for 2 hours at 80°C followed by a post cure at 175°C for at least 15 hours. The cured bars were removed from the mould while still hot as it was then easier to release the samples. Each set of bars was made up using an identical procedure, therefore any errors incurred will be consistent and still allow data trends to be compared.

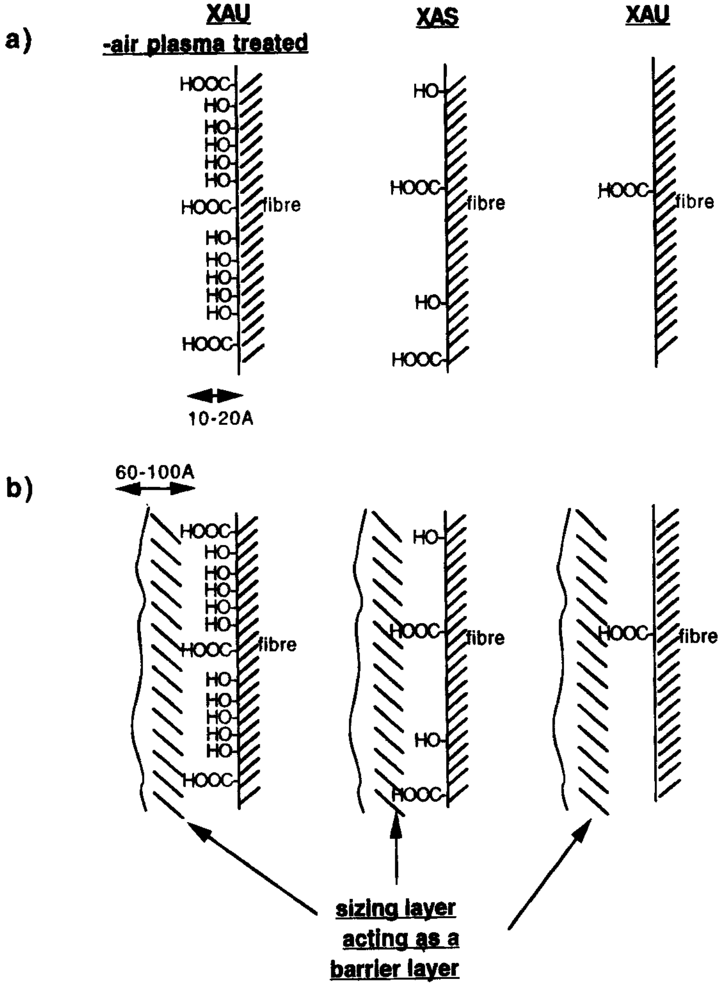

FIGURE 1 Schematic diagrams of the fibre surfaces: a) without and b) with sizing.

Interlaminar Shear Testing

Short beam shear tests were carried out to determine the level of fibre/matrix adhesion between the different fibre surfaces and the two resin systems. The short beam shear tests carried out on the anhydride resin system samples were done in accordance with the CRAG testing method.[17] Those carried out on the amine resin system have been reported elsewhere[9] and were in accordance with BS 2782.[18] Both the British Standard and the CRAG test method are designed to induce shear failure along the neutral axis of the composite sample.

Fracture surfaces were examined using a Hitachi S2460N scanning electron microscope.

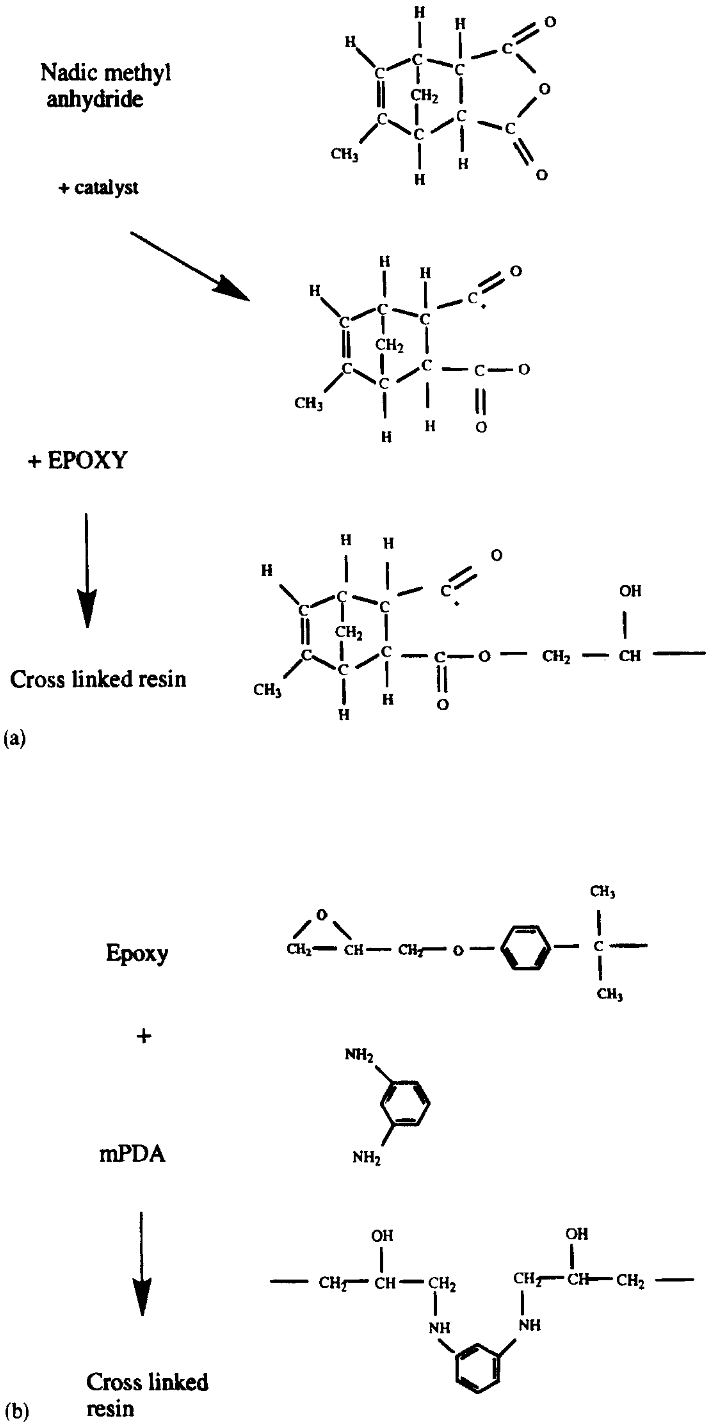

FIGURE 2 Curing reactions for: a) anhydride-cured resin system b) amine-cured resin system.

DMTA Testing

Dual cantilever bending mode DMTA was carried out using a Polymer Laboratories Mk I analyzer. Samples from the composite bar were cut into lengths of approximately 35 mm and ground to a thickness of between 0.5 mm and 1 mm. Tests were carried out over a sample free length of 10 mm. Samples were heated at a rate of 2°C/min to minimize errors due to thermal lag as explanied by Thomason *et al.*[6] A strain rate was chosen that gave a nominal displacement 64 μm which ensured that interfacial failure did not occur during testing. A single frequency scan was carried out at a frequency of 1 Hz over a temperature range to include the glass transition.

Single cantilever bending DMTA was carried out on a Polymer Laboratories Mk II analyzer. Heating rate, strain rate and frequency were identical to those used for dual cantilever testing; however, the sample thickness was approximately 2 mm and the sample free length was varied. The loading conditions are shown schematically in Figure 3. Samples in which the fibres were aligned in the longitudinal, *i.e.* parallel to the length of the bar, and in the transverse direction were tested.

Differential Scanning Calorimetry (DSC)

DSC was carried out on the cured samples using a Thermal Analysis DSC10 analyzer. Scans were carried out between 80°C and 220°C at a heating rate of 10°C/min while the system was constantly being purged with oxygen-free nitrogen.

RESULTS

Anhydride-Cured Resin System

Short Beam Shear Test

The interlaminar shear strength (ILSS) values for composite samples made from fibres with the various fibre surface treatments are shown in Table II. The values obtained for

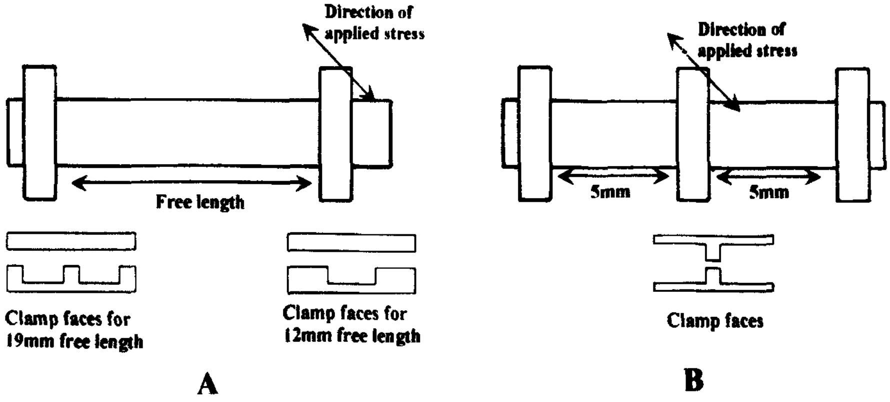

FIGURE 3 Loading conditions for DMTA A) Single cantilever B) Dual cantilever.

TABLE II
Anhydride system ILSS results
(one standard deviation shown in brackets)

Sample	ILSS (MPa)
XAU fibre composite	64.2(3.0)
XAS fibre composite	72.1(2.9)
Air plasma fibre composite	71.0(2.7)

XAS and air-plasma-treated XAU are very similar (~72 MPa), indicating that air plasma treatment improves fibre/resin adhesion. These values are comparable with those obtained using the amine-cured resin reported previously.[2] The fracture surfaces of all samples were examined using scanning electron microscopy. As expected, a large amount of fibre pull-out was observed on the fracture surfaces of composites made using XAU fibres. Despite the similar ILSS values, the fracture surfaces of samples made from XAS and air-plasma-treated XAU fibres appeared quite different, as shown in Figure 4. The XAS fibre sample shows a large amount of resin adhering to the fibre surface after fracture, whereas the air-plasma-treated fibre composite shows significant fibre pull-out with less resin adhering to the fibre surface. These fracture surfaces are very similar to those obtained from testing composites using the amine-cured resin system. It has already been shown that the improvement in adhesion observed as a result of surface treatment is due to quite different phenomena when comparing electrochemically-treated fibres with those that have been exposed to an air plasma.[2] For XAS fibres it has been shown that weakly bound crystallites are removed from the surface, leaving a more mechanically superior surface to which the resin can adhere.[1] Rather than removing surface layers, plasma treatment introduces a large concentration of functional groups onto the outermost layers of the fibre surface which have the potential to interact with the resin. It is possible that this leads to the different fracture behaviour in these two samples. Further evidence, however, is required to support this postulation.

Dynamic Mechanical Thermal Analysis (DMTA)

The measurement of tan δ involves a geometry factor which takes into account the free length of the sample and the mode of clamping. However, the geometry factor does not take into account the area of the sample under the clamps and the thermal conductivity of the sample. In the dual cantilever mode, the ratio of length of clamped sample to effective free length is relatively high. The temperature of the sample is measured by means of a transducer placed immediately behind the sample between the cantilever arms. In dual cantilever the actual temperature recorded by this transducer is lower than that expected by the instrument since the metal clamps transfer heat away from the sample. This can lead to large discrepancy between the actual sample temperature and that registered by the instrument. In single cantilever the fraction of sample under the clamps is less and, therefore, there is less of a difference between the actual sample temperature and that determined by the instrument as a result of the predetermined heating rate. This offers an explanation for the differences in measured T_g between dual

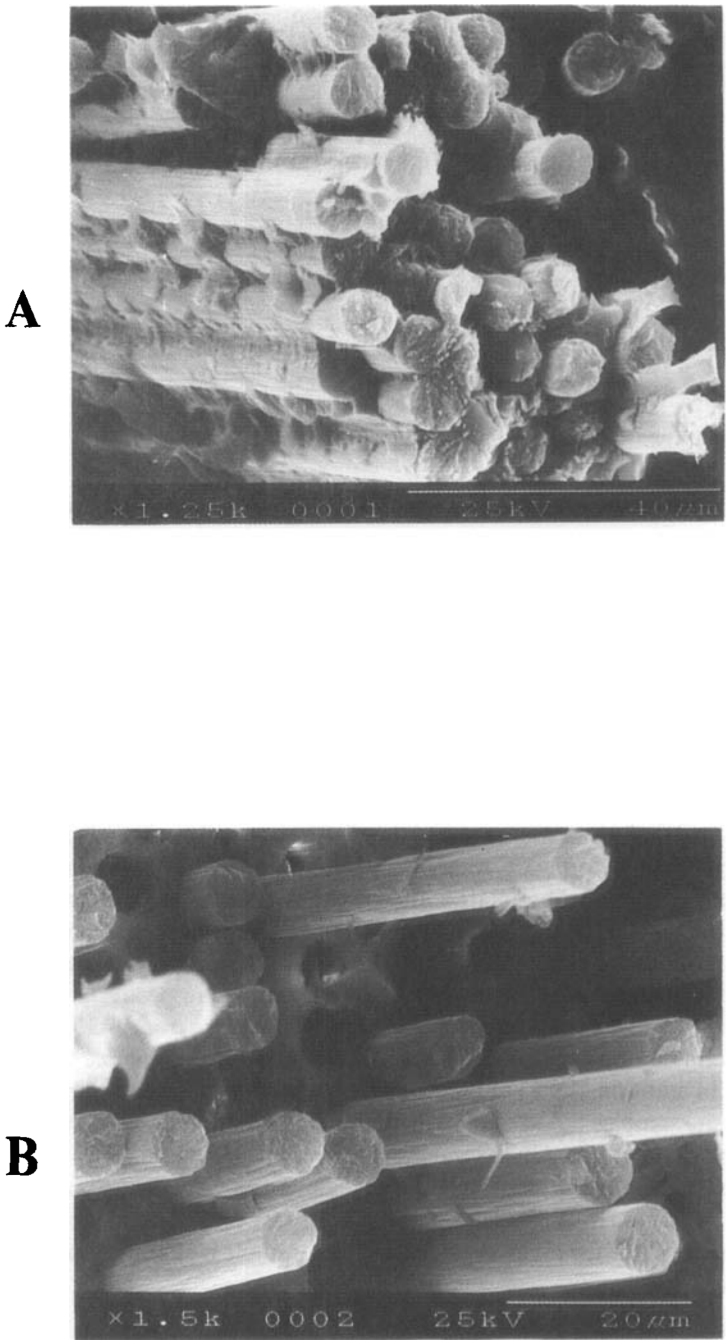

FIGURE 4 SEM images of fracture surfaces from the short beam shear test A) XAS fibre sample B) Air-plasma-treated fibre sample.

TABLE III
Effect of testing mode on T_g, as measured from tan δ, for longitudinal anhydride-cured samples

Testing mode	RESIN	XAU	XAS	Air plasma
Dual cantilever free length 12 mm (T_g °C)	135	177	–	–
Single cantilever free length 12 mm (T_g °C)	143.5	176	167	165.5
Single cantilever free length 19 mm (T_g °C)	143	174	169	161.5

cantilever and single cantilever mode testing as shown in Table III. The 8.5°C differnece for the pure resin sample is much greater than the 1°C difference for the longitudinally-oriented XAU composite sample, as the thermal conductivity of the resin is much lower than that of the composite sample. The high conductivity of the composite sample results in a quicker and more uniform distribution of temperature within the sample.

Both longitudinal and transversely oritented fibre samples were tested in single cantilever bending. It was expected that for transversely-oriented samples the matrix properties would dominate, whereas for longitudinal samples the data would be more representative of the fibre/matrix interphase. This seemed to be borne out in the data obtained. Figures 5a and b compare the tan δ *vs* temperature response for pure resin and composite samples made from XAU, XAS, and air-plasma-treated XAU fibres for longitudinally and transversely oriented fibre samples, respectively. Addition of XAU fibres to the resin causes an increase in the measured T_g from 143°C to 174°C for the longitudinal sample, whereas for the transversely-oriented sample the T_g increases to 164°C. In addition, there is a marked difference in the value of T_g for the three types of composite samples tested in the longitudinal direction. However, this is not apparent from the samples tested in the transverse direction. The values of T_g from longitudinal samples loaded in the single cantilever regime using different span lengths are also shown in Table III. A similar trend for both sets of data is observed; however, the decrease in T_g for the air-plasma-treated fibre sample is slightly more pronounced for the longer free length.

Differential Scanning Calorimetry (DSC)

The trends in T_g mentioned in the previous section are confirmed by the DSC data collected from identical samples, although the variation is not as large (see Table IV). This is expected since this technique is measuring data which are representative of the whole sample and trends due to the interface properties will be overshadowed

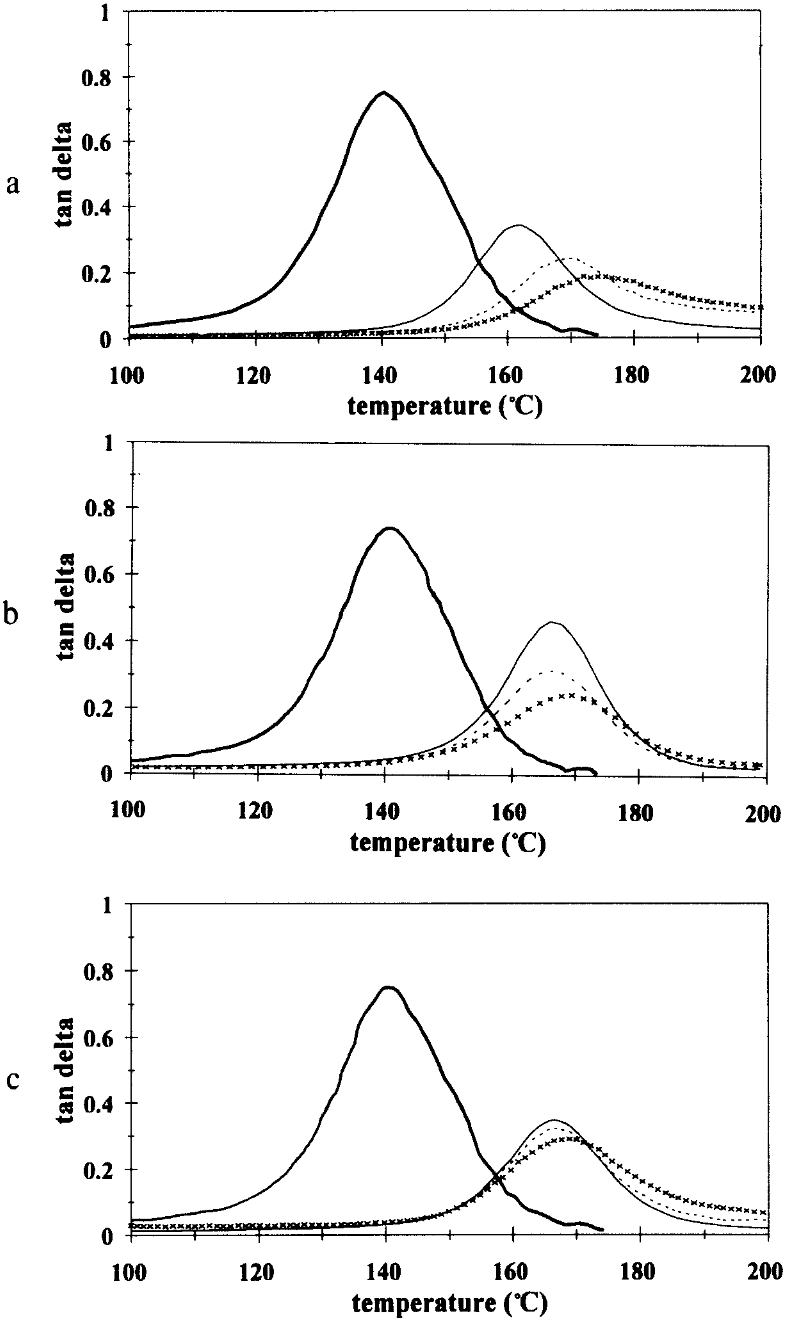

FIGURE 5 Tan δ curve for *anhydride* cured samples, showing effect of fibre addition, sample free length 19mm a) longitudinally-oriented fibre samples b) transversely-oriented samples c) sized, longitudinally-oriented fibre samples. Legend—resin × × XAU fibre composite, ''' XAS fibre composite, — Air-plasma-treated fibre composite.

TABLE IV
Anhydride system DSC results

Sample	T_g (°C)
Unfilled resin	150
XAU fibre composite	159
XAS fibre composite	157
Air plasma fibre composite	154

somewhat by data from the bulk matrix. The addition of fibres causes an increase in T_g from 150°C to 159°C and the effect of different surface treatments is also apparent.

The Effect of Sizing

All three types of fibre were coated with a thin layer of epoxy prior to their incorporation into the anhydride-cured resin system. An increase in T_g to approximately 168°C was observed over that of the pure resin (143°C), which was irrespective of fibre surface chemistry. These data are presented in Figure 5c. The full width at half maximum (FWHM) of the tan δ curve also decreases from 40°C for the unsized XAU fibre samples to 21°C for the sized XAU fibre samples.

Amine-Cured System

The glass transition temperature for the unfilled resin was measured as 175°C. This is significantly higher than that obtained for the anhydride system. It was found that neither the addition of the fibres nor the nature of the fibre surface treatment significantly affected the T_g, which remained at values between 175–179°C, as shown in Table V. This is confirmed in the DSC results also shown in Table V.

DISCUSSION

The measured T_g values for the anhydride and amine epoxy systems are 143°C and 175°C, respectively. The addition of carbon fibres only affects the T_g of the anhydride-cured resin. If, as Thomason[6] suggested, such increases are primarily due to the differences in thermal conductivity of the samples, then a similar increase would be

TABLE V
T_g measured from DMTA and DSC for amine-cured samples

Sample	T_g from DMTA (°C)	T_g from DSC (°C)
Unfilled resin	175	175
XAU fibre composite	178	174
XAS fibre composite	178	175
Air plasma fibre composite	179	173

expected for the amine-cured composite samples. The effects of surface treatment would also not be observed, as the volume fraction of fibres was the same in each case and, hence, the thermal conductivities of the samples were identical.

If the affected area was a discrete region with a different T_g from the bulk resin then two maxima would be observed in the $\tan\delta$ curve. This is not the case. The curve for the longitudinally-oriented XAU composite is very broad, having a FWHM of approximately 40°C compared with a value of 18°C for the pure resin. The curve for the transversely-oriented sample is also broader than for the pure resin (FWHM 23°C). The width of the curve gives an indication of the range of transition temperatures measured. It, therefore, suggests that the restriction of molecular motion within the anhydride-cured resin due to the addition of untreated fibres is a *long-range* effect.

The nature of the fibre surface also affects the localised curing of the anhydride system. The concentration of functional groups on the fibre surface is greatest for air-plasma-treated fibres and follows the trend air-plasma-treated XAU > XAS > XAU. This negative effect on curing by the presence of functional groups has also been observed by Gerard[4] and Peret *et al.*[9] In both cases, however, they did not observe the increase in T_g due to the presence of the fibres themselves. Several reasons why these groups affect the localised curing of the resin have been proposed by other research groups.[9,14,15] Some of these will now be discussed.

The chemical groups present on the fibre surface, *i.e.* carboxylic acid and keto-enols,[2] are both capable of reacting with the resin constituents. Chemical interactions at the interface will result in a localised stoichiometry imbalance and, therefore, a lowering of the cross-link density within the interphase region. This would result in a lowering of the T_g. This effect would be greatest for the air-plasma-treated fibres, which is indeed the case. If it were the epoxy molecule that was preferentially adsorbed, as proposed by Ko,[7] a similar effect would be observed in both systems; however, fibre surface chemistry appears to have no effect on the localised curing of the amine/epoxy system. Garton *et al.*[12] proposed that it was preferential adsorption of the catalyst onto the oxidised sites on the fibre surface that results in a change in the T_g. The catalyst used by Garton and in our experiments is a tertiary amine. It is also a possibility that preferential adsorption of the anhydride is responsible for the localised stoichiometry imbalance.

Another feasible explanation is that the presence of acid and keto-enol groups alters the pH close to the fibre surface. This, in turn, would affect the localised curing of the resin. Once again, the most pronounced effect would be observed for the air-plasma-treated fibres. Unfortunately, we have not able to determine which, if either, of these mechanisms is responsible for the observed changes in interphase properties.

By sizing the fibres prior to their incorporation into the matrix, a barrier layer is introduced between fibre and resin acting to inhibit the effects due to the presence of functional groups on the fibre surface. The sizing layer is too thin to produce a secondary $\tan\delta$ peak as observed by Harris *et al.*[3] and Dibenedetto and Lex,[15] but it does lower the T_g from 174°C to 168°C in the case of XAU fibre, and a reduction in the FWHM of the $\tan\delta$ peak is observed. This suggests that the sizing layer also reduces the effect of the restriction imposed by the fibre surface.

CONCLUSIONS

The presence of fibres has no effect on the localised curing of an *amine*-cured epoxy resin composite. Fibre addition can, however, affect curing of an *anhydride*-cured epoxy resin system. In addition, the concentration of chemical groups on the fibre surface influences the observed changes in the T_g. It is proposed that two counteracting effects occur in the anhydride system: the presence of the fibres causes the restriction of molecular motion, and the presence of functional groups on the fibre surface acts to reduce the cross-link density close to the fibre surface. The former increases the T_g whereas the latter results in a decrease. This is a interphase phenomenon, since these changes are only observed when the samples are tested in the longitudinal direction and not in the transverse direction where bulk matrix properties dominate.

The presence of an epoxy size on the fibres acts as a barrier to any fibre/resin interactions occurring and the measured T_g is similar irrespective of fibre treatment.

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