

Thermomechanical behaviour of interfacial region in carbon fibre/epoxy composites

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A study of the thermomechanical stability of the fibre-matrix interphase in carbon/epoxy composites has been carried out. The thermodynamic work of adhesion has been evaluated at room temperature by wetting measurements. The interfacial shear stress transfer level (τ) for sized and desized carbon fibre has been measured as a function of temperature by means of a single-fibre fragmentation test. As the test temperature increased (τ) values were found to decrease, with values being higher for the desized carbon fibre. The dependence of interfacial shear stress transfer on bulk matrix mechanical properties (modulus and shear strength) has also been discussed. Dynamic mechanical measurements performed on single-bundle composites confirmed the better thermomechanical stability of the desized fibre interphase. Copyright © 1996 Elsevier Science Limited

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INTRODUCTION

In the last few years a great deal of effort has been expended to understand the influence of interfaces and interphases on the mechanical behaviour of composite materials. Several experimental methods¹⁻³ have been developed to characterize the fibre-matrix interactions and a lot of work, both theoretical⁴⁻⁷ and experimental⁷⁻¹⁵, has been done to obtain the structure-property relationships between fibre-matrix adhesion and composite mechanical properties. It has been shown for example, that in unidirectional graphite/epoxy composites the level of adhesion between fibres and matrix mainly affects both in-plane and interlaminar shear strengths⁸, the longitudinal and transverse tensile and flexural strengths⁹, the longitudinal compressive strength¹⁰, and the mode II fracture toughness¹¹. All these mechanical properties were found to be improved as the interfacial adhesion increased. High composite strength requires a strong interfacial bond, but this may lead to a low total fracture energy absorption¹⁵. However, by optimization of the physical and mechanical properties

of the fibre-matrix interface, both high strength and high toughness characteristics can be achieved simultaneously⁷. Of course, this task can be attained only through a deep understanding of the main parameters involved in the mechanism of stress transfer from matrix to fibre.

Among the numerous parameters affecting the interfacial adhesion in a polymer matrix composite, the temperature plays a major role. Nevertheless, in the literature only little experimental work has been done towards understanding the effect of temperature on the interfacial behaviour. The thermomechanical stability of the interfacial region in polymeric composite materials, both thermosetting and thermoplastic, has been mainly studied on single-fibre microcomposites using the fragmentation test¹⁶⁻²⁴ and the pull-out test²⁵. One interesting point concerns the relationship between the matrix yield properties and the capacity to transmit interfacial shear stresses. Some authors found interfacial shear strength values higher than the shear strength of the bulk matrix¹⁶⁻¹⁹, while others found that the interphase thermomechanical stability was lower or equal to that of the bulk resin^{16,20}. Some efforts to obtain more information about the thermal behaviour of the interphase have even been done using dynamic

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mechanical thermal analysis^{26–35} (d.m.t.a.) in composites with a high fibre volume fraction.

The objective of this paper is to investigate the thermomechanical behaviour of the interfacial region in carbon/epoxy composite systems using both the fragmentation test on single-fibre microcomposites and d.m.t.a. measurements on single-bundle composites.

EXPERIMENTAL

Materials

Carbon fibres Besficht HTA-7-3000 from Toho Rayon Co. Ltd were used for the present work. The fibres supplied by the manufacturer were surface treated and coated with 1.37 wt% of an epoxy-compatible sizing agent whose main component was bisphenol-A type epoxy resin. The filaments were used either in the as received state (AR fibres), or desized (ARD fibres) by extraction for 6 h in a Soxhlet apparatus using toluene as solvent³⁶. Desizing was followed by washing in ethyl acetate and drying in vacuum at 100°C.

From SEM observation the fibres have a circular cross-section and their diameter was measured using an optical microscope and an image analyser system. From 50 measurements on different fibres the diameter was found to be $7.0 \pm 0.7 \mu\text{m}$.

The epoxy matrix used in this work was a diglycidyl ether of bisphenol-A (Eposir 7120, SIR SpA) cured with 24 phr by weight of isophorone diamine (ID 01784, SIR SpA). After mixing and stirring the resin was defoamed in vacuum, cured at 60°C for 2 h, followed by 2 h at 140°C and allowed to cool slowly to room temperature by shutting off the oven. Differential scanning calorimetry (d.s.c.) measurements performed with a Mettler DSC 30 apparatus confirmed the complete conversion of the resin and indicated a glass transition temperature T_g equal to 152°C. All the specimens (bulk matrix, single-fibre microcomposites and single-bundle composites) were cured as described above.

Fibre properties

As suggested by the fibre manufacturer, the amount of sizing actually present on the AR fibres was determined following the thermal decomposition method described in JIS Standard R7601-86. The test was performed by measuring the weight loss of two test pieces weighing ~ 5 g, after exposure at 450°C for 15 min in flushing nitrogen.

The chemical composition of the fibre surface, both as received and desized, was examined by means of X-ray photoelectron spectroscopy (X.p.s.) measurements performed with a Kratos Axis-HS instrument, using a Mg excitation source ($h\nu = 1253.3 \text{ eV}$). The samples were analysed with the hemispherical analyser (pass energy of 40–80 eV).

The strengths of the fibres were measured, at four different gauge lengths of 5, 10, 15 and 20 mm, on

monofilaments carefully extracted from a bundle by following the ASTM Standard D3379-75. By using an Instron 4502 tensile tester equipped with a 10 N load cell, tests were conducted at room temperature and at a constant cross-head speed of 0.2 mm min^{-1} . As suggested by Asloun *et al.*³⁷ at least 25 monofilaments were tested for each gauge length. Assuming that the strength of a fibre obeys the Weibull weakest link model³⁸, the mean strength as a function of fibre length $\bar{\sigma}_{f_b}(L)$ is given by

$$\bar{\sigma}_{f_b}(L) = \alpha L^{-1/\beta} \times \Gamma\left(1 + \frac{1}{\beta}\right) \quad (1)$$

where α and β are the Weibull scale and shape parameters, respectively, L is the fibre length and Γ is the gamma function. The plot $\ln[\bar{\sigma}_{f_b}(L)]$ versus $\ln(L)$ produced a straight line whose gradient was $-1/\beta$ and whose intercept was

$$\ln \alpha + \ln \left[\Gamma\left(1 + \frac{1}{\beta}\right) \right] \quad (2)$$

which allowed us to evaluate α . The applicability of the two-parameter Weibull analysis to carbon fibre is well demonstrated in the literature³⁹.

Matrix properties

The mechanical properties of the bulk matrix were determined by using an Instron 4502 tensile tester equipped with a thermostatic chamber (model 3119) and an extensometer (model 2620) for the tensile modulus measurements. All the experimental points represent the average value obtained from five dog-bone shaped specimens whose dimensions are reported in Figure 1. The specimens were prepared by pouring the defoamed catalysed resin into a plasticine mould. The strength property relevant to a discussion of the fibre–matrix interfacial shear strength is, of course, the shear strength of the resin, and although we have not measured this directly, the matrix shear strength τ_m may be estimated^{14,40} from the matrix tensile strength σ_m using the von Mises relationship, $\tau_m = \sigma_m/\sqrt{3}$.

Contact angle measurements

Contact angles were measured using a Dynamical Wilhelmy Microbalance model 322 (Cahn); this microbalance, which is fully automated and computer

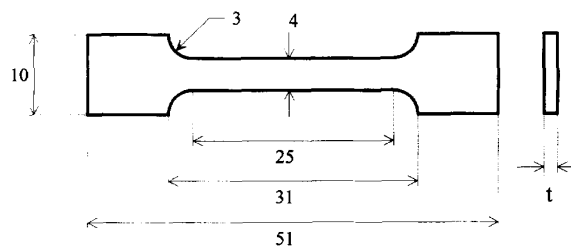


Figure 1 Dimensions (mm) of dog-bone shape specimens used for bulk matrix mechanical properties measurements ($t = 2 \text{ mm}$) and single-fibre microcomposite ($t = 1 \text{ mm}$)

controlled, has a precision of $\pm 1 \mu\text{g}$ and a variable immersion speed (range $2\text{--}256 \mu\text{m s}^{-1}$).

At first, we tried to measure the contact angles in five liquids, namely water, methylene iodide, glycerol, formamide and dimethylsulfoxide, in order to perform a three component acid–base analysis of surface tension⁴¹. Unfortunately, due to fibre and matrix solvent absorption, no appropriate combination of the same three liquids worked well. To avoid any possible error due to the use of different wetting liquids for fibres and matrix, we decided to use only two solvents, obtaining a two-component analysis of surface tension and adhesion work, using the harmonic and geometric mean equations⁴². Water (HPLC grade from Merck) and methylene iodide (RPE 99% from Acros) were used as contacting liquids and their surface tensions were measured using a glass plate, whose surface was activated in air plasma at 100 J s^{-1} for a few minutes. A speed of $21 \mu\text{m s}^{-1}$ has been used for the fibres and epoxy resin samples. The immersion depth and the environmental test chamber temperature were equal to 20 mm and $20.0 \pm 0.1^\circ\text{C}$, respectively. At least five specimens have been tested for each experimental situation.

Interfacial shear stress transfer level

The interfacial shear stress transfer level ($\langle\tau\rangle$) has been evaluated through the fragmentation test and following the simplified physical model proposed by Kelly and Tyson⁴³, which yields the well known expression

$$\langle\tau\rangle = \frac{d\bar{\sigma}_{f_b}(L_c)}{2L_c} \quad (3)$$

where d is the fibre diameter, L_c the critical length and $\bar{\sigma}_{f_b}(L_c)$ is the mean fibre strength at the fibre critical length. The critical length was taken to be equal to $4.3 \bar{L}_s$, where \bar{L}_s is the mean fragment length measured at saturation.

The interfacial shear stress transfer level was evaluated at various temperatures using a custom-made apparatus for the fragmentation test¹⁶, consisting of a small tensile tester (Minimat from Polymer Laboratories), equipped with a thermostatic chamber, and put under a polarized optical stereo-microscope (Leica-Wild M3Z). Events were recorded during the test using a Sony B/W video camera mounted on the microscope and a video recorder. The tests were stopped at a strain of ~ 0.06 , which allowed us to reach saturation of the fragmentation process before sample breakage. Each experimental point represents the average value of at least three single-fibre microcomposites containing one single fibre completely embedded along the centre-line of a dog-bone shape specimen, the dimensions of which are shown in Figure 1.

The shear stresses at the interface arising from thermal and Poisson shrinkages were computed as described in the Appendix.

Dynamic mechanical properties

Dynamical mechanical thermal analysis (d.m.t.a.) was performed in tensile mode using a Polymer Laboratories DMTA Mk II (Loughborough, UK) instrument. D.m.t.a. measurements were carried out on strips ($15 \text{ mm} \times 4 \text{ mm} \times 1 \text{ mm}$) of bulk matrix and on strips ($15 \text{ mm} \times 2.5 \text{ mm} \times 0.8 \text{ mm}$) of single-bundle composite (SBC) specimens prepared as follows. A fibre bundle $\sim 200 \text{ mm}$ in length was immersed in the catalysed resin, gently squeezed to exclude excess resin, and cured. The fibre content of the SBC specimens (determined from gravimetric measurements) was constant for all the specimens and equal to 9.5% by weight or 6.5% by volume.

Both for the bulk matrix and for the single-bundle composites, an apparent activation energy ΔE for the glass transition has been calculated, as reported by other authors^{26,30,34,44}, using the following Arrhenius equation

$$\omega = A \exp(-\Delta E/RT_g) \quad (4a)$$

where ω is the test frequency, T_g is the absolute temperature at the glass transition loss factor peak and A is a frequency factor. A regression line plot of $\ln \omega$ versus $1/T_g$ enabled the activation energy ΔE to be calculated from the equation

$$\ln \omega = \ln A - \Delta E/RT_g \quad (4b)$$

RESULTS AND DISCUSSION

From the thermal decomposition method, the amount of sizing on the AR fibres was found to be equal to $1.41 \pm 0.9 \text{ wt}\%$, in good agreement with the manufacturer's specification. By assuming a density of 1.16 g cm^{-3} and 1.77 g cm^{-3} for the DGEBA resin and for the carbon fibre, respectively, we estimated a sizing thickness equal to 37.5 nm. The solvent desizing procedure caused a weight loss equal to $1.58 \pm 0.03 \text{ wt}\%$ and consequently we could assume that most of the sizing had been removed from the fibres. The results of X.p.s. measurements are reported in Table 1. As already reported in the literature⁴⁵ for the same fibre, a remarkable presence of oxygen was found on the AR fibre. After desizing in boiling toluene the surface of the fibre showed at 20% decrease in oxygen content and slight variation in the concentration of other elements (Si, N).

Table 1 X.p.s. analysis of as received (AR) and desized (ARD) Besight HTA-7-3000 carbon fibre

Fibre	O (at%)	Si (oxide) (at%)	N (at%)	Notes
AR	20	2	1	Most of the oxygen bonded to carbon
ARD	16	1	1.4	Little Ca, sputtering shows a thin layer of oxygenated Si

Table 2 Advancing (θ_{adv}) and receding (θ_{rec}) contact angles measured in water and in methylene iodide

Material	Contact angles in water		Contact angles in methylene iodide	
	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}
Epoxy resin	84 ± 2	47 ± 5	45 ± 1	0
AR fibre	64 ± 3	50 ± 6	40 ± 1	24 ± 4
ARD fibre	60 ± 3	49 ± 3	34 ± 2	24 ± 4

Table 3 Total surface energy γ and its dispersive and polar components γ^d and γ^p , respectively, calculated from experimental advancing contact angles by harmonic and geometric mean methods

Material	Surface energies (mJ m ⁻²): Harmonic mean method			Surface energies (mJ m ⁻²): Geometric mean method		
	γ	γ^d	γ^p	γ	γ^d	γ^p
Epoxy resin	41.9	34.5	7.4	37.2	34.1	3.1
AR fibre	52	36	16	45	32	13
ARD fibre	56.2	38.6	17.6	48.5	34.2	14.3

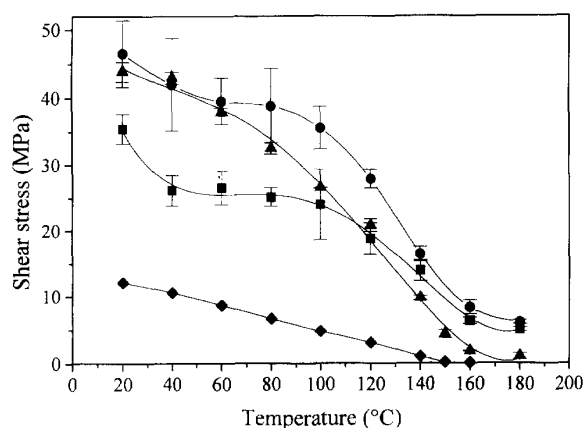
Table 4 Total adhesion work W and its dispersive and polar components W^d and W^p , respectively, evaluated from the surface energies reported in Table 3

Material	Adhesion work (mJ m ⁻²): Harmonic mean method			Adhesion work (mJ m ⁻²): Geometric mean method		
	W	W^d	W^p	W	W^d	W^p
AR fibre/epoxy	90.7	70.5	20.2	78.8	66.1	12.7
ARD fibre/epoxy	93.7	72.9	20.8	81.6	68.3	13.3

Advancing and receding contact angles for the epoxy resin and the carbon fibres before (AR) and after (ARD) the extraction in toluene are reported in Table 2. The values of advancing contact angles in water and in methylene iodide are only slightly lower for ARD than for AR fibre, thus indicating a corresponding small enhancement of dispersive component. Nevertheless this difference is so small that we can conclude that the extraction procedure in toluene did not remove the whole amount of sizing from the AR fibres, but probably reduced its thickness, still leaving a thin layer of coating on the fibre surface.

Contact angle measurements obtained in two different liquids (water and methylene iodide) allowed us to evaluate the fibre and epoxy surface energies (Table 3). Using these surface energy data, it was possible to determine the values of the thermodynamic work of adhesion between fibre and matrix, as reported in Table 4.

From values of adhesion work and their components we can say that the driving force for adhesion is the difference in polar components between the fibres and matrix; the level of thermodynamic work of adhesion is substantially the same for both systems, and consequently any possible variation in the stress transfer at the interface should be attributable to the different mechanical properties of the interphase.


Figure 2 Effect of temperature on interfacial shear stress transfer level, for AR (■) and ARD (●) carbon fibre, on matrix shear strength (▲) and on frictional shear stress (◆)

The Weibull parameters for the tensile strength of the carbon fibres tested in air resulted in $\alpha = 5.949$ and $\beta = 4.8$ for the AR fibres, and $\alpha = 5.711$ and $\beta = 5.0$ for the ARD fibres. The scale parameter α of the desized fibres was only slightly lower than that for the as received fibres, but the shape parameter β was slightly higher. So, following equation (1), the mean fibre tensile strength results were practically unchanged after the desizing procedure. In previous work¹⁶ we measured the Weibull parameters for the tensile strength of the same AR carbon fibres embedded in an epoxy matrix, using the continuously monitored single-filament composite (CM-SFC) test developed by Yavin *et al.*⁴⁶, obtaining $\alpha = 5.482$ and $\beta = 5.0$. Although very similar, the parameters obtained with the continuously monitored procedure are probably more appropriate because they were obtained using strength data closer to the critical length and because the fibres were tested directly in the matrix.

The temperature dependence of the interfacial shear stress transfer level (τ) obtained on microcomposites containing either as received or desized carbon fibre is reported in Figure 2. For comparison, in the same figure we report the estimated shear strength values of the bulk matrix as a function of temperature. As reported by other authors¹⁶⁻²⁴ we found a decrease of stress transfer level as the temperature was raised. The values of (τ) for the desized fibres were significantly higher than those for the sized fibres. This behaviour can be explained by supposing that the fibre sizing led to an interphase with mechanical properties lower than that of the bulk matrix while, by reducing the sizing thickness, the interphase can exhibit mechanical properties similar to those of the bulk matrix. This explanation is supported by the fact that, at temperatures lower than 120°C, experimental (τ) values for sized fibres are lower than the bulk matrix shear strength, and at higher temperatures we obtained (τ) values slightly higher than the shear strength of the bulk matrix (Figure 2). Moreover, for the desized fibres (τ) values were equal to (up to 80°C) or greater than the shear strength of the bulk matrix. It is worth noting that

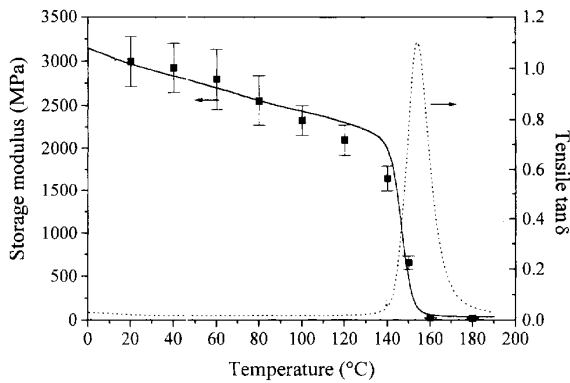


Figure 3 Matrix tensile storage modulus (—) and loss factor (···) at test frequency of 5 Hz versus temperature. In the same plot the temperature dependence of the static tensile modulus (■) of the bulk matrix is also reported

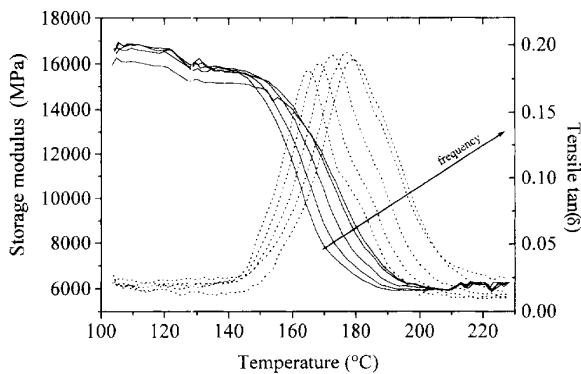


Figure 4 Tensile storage modulus and loss factor at various frequencies (1, 2, 10, 30, 50 Hz) versus temperature for AR fibre single-bundle composites

with the same sized fibres embedded in a more flexible epoxy matrix (T_g equal to 39°C), we found¹⁶ $\langle\tau\rangle$ values higher than the bulk matrix shear strength, but after fibre desizing (τ) values decreased to values almost equal to the shear strength of the bulk matrix. In *Figure 2* we also report the shear frictional stresses τ_f due to thermal and Poisson shrinkages of the bulk matrix as a function of temperature, evaluated as described in the Appendix.

Frictional stress plays an important role in determining the interfacial adhesion, especially at room temperature,

and becomes less and less important as the temperature increases. The values of the tensile modulus of the matrix used in the analytical evaluation of the frictional stresses are reported in *Figure 3* as a function of temperature. In the same figure the temperature dependence of the conservative modulus and the loss factor of the bulk matrix are reported, as measured by means of the d.m.t.a. in the tensile mode. It can be seen that a good agreement exists between the static and the dynamic tensile modulus measurements. It is worth noting that in *Figure 2* and for both types of systems, a transition seems to appear near room temperature in the variation of $\langle\tau\rangle$, whereas this is not the case for the variations of matrix tensile modulus (*Figure 3*). This behaviour could be tentatively explained by supposing the existence of an interphase of lower glass transition temperature than the bulk matrix, as already observed by other authors^{21,22}.

The thermomechanical behaviour of the interfacial bond strength has also been studied by means of dynamic mechanical thermal analysis performed on single-bundle composites in the tensile mode. Typical d.m.t.a. thermograms for the bulk matrix and single-bundle composites are reported in *Figure 3* and *Figure 4*, respectively, whereas the numerical values are reported in *Table 5*. The restriction of polymer chain movement due to the presence of reinforcing fibres leads to a strong reduction in $\tan\delta$ peak and to an increase in glass transition temperature measured as the temperature corresponding to the $\tan\delta$ peak. As can be seen from *Table 5*, a different interphase structure causes a difference in dynamic mechanical behaviour. Accordingly to the principle²⁹ that a composite with a poor matrix–fibre load transfer tends to dissipate more energy than one with good interfacial interaction, the $\tan\delta$ peak of AR composites was higher than that of ARD composites. From the T_g values at the $\tan\delta$ peak it is possible to obtain a further confirmation of the lower thermomechanical stability of the interphase resulting from sized fibre. In fact, at all the test frequencies, T_g values of AR fibre composites were lower than those of ARD composites.

According to equation (4b), by plotting the logarithm of the test frequency versus the reciprocal absolute temperature corresponding to the $\tan\delta$ peak, the activation energy for the glass transition can be calculated from the slope of the regression line. *Figure 5* presents

Table 5 Loss factor peak ($\tan\delta$) and corresponding temperature from d.m.t.a. measurements performed in tensile mode, at various frequencies, at heating rate of 1°C min^{-1}

Frequency (Hz)	Bulk matrix		Single-bundle composite with AR fibre		Single-bundle composite with ARD fibre	
	Tan δ peak	Temperature at tan δ peak ($^\circ\text{C}$)	Tan δ peak	Temperature at tan δ peak ($^\circ\text{C}$)	Tan δ peak	Temperature at tan δ peak ($^\circ\text{C}$)
1	1.1372	152.8	0.1803	164.1	0.1648	170.2
3	1.1148	156.0	0.1865	168.4	0.1672	174.3
10	1.0906	159.0	0.1924	172.7	0.1729	177.1
30	1.0705	162.2	0.1943	176.9	0.1743	181.2
50	1.0582	164.5	0.1891	179.6	0.1656	182.8

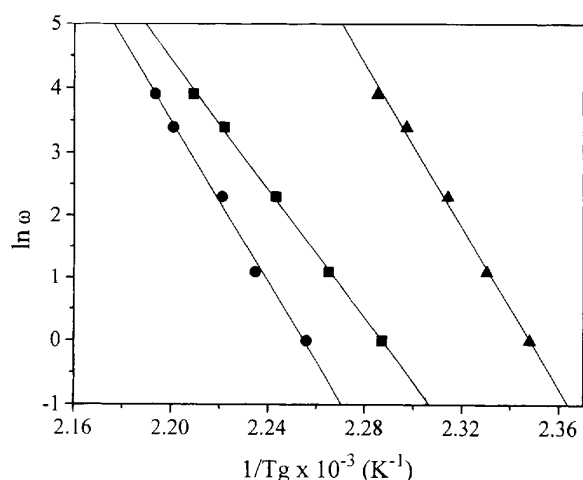


Figure 5 Logarithm of test frequency versus reciprocal absolute temperature of glass transition for the bulk matrix (▲), and for AR (■) and ARD fibre (●) single-bundle composites

Table 6 Activation energies for glass transition obtained from d.m.t.a. measurements

Sample	Activation energy, ΔE (kJ mol ⁻¹)
Bulk matrix	530
Single-bundle composite with AR fibre	424
Single-bundle composite with ARD fibre	527

this relationship, and the calculated values for the activation energy are given in Table 6. It can be seen that the relaxation of the AR fibre composites requires less energy compared with the bulk matrix. This behaviour can be attributed to the presence of a 'soft' interphase due to the sizing of the AR fibres. This explanation is confirmed by the energy value obtained for the activation of glass transition in single-bundle composites with ARD fibres. In fact, following desizing, the value of ΔE almost returns to that obtained for the bulk matrix.

CONCLUSIONS

The effect of temperature on the fibre-matrix interfacial shear stress transfer level ($\langle\tau\rangle$) for an epoxy matrix reinforced with sized (AR) or desized (ARD) carbon fibres was studied. Gravimetric measurements showed that the toluene extraction procedure used for fibre desizing resulted in the removal of most of the sizing coating, whereas wetting measurements indicate that a thin sizing layer is still present on the ARD fibres, because the thermodynamic work of adhesion with the epoxy resin did not change substantially after toluene extraction.

The results obtained by means of the single-fibre fragmentation test indicate that $\langle\tau\rangle$ values decreased as the test temperature increased. The values of $\langle\tau\rangle$ for the desized fibres were significantly higher than those obtained with the sized fibres. By comparison with

bulk matrix mechanical properties, the $\langle\tau\rangle$ values for the AR and ARD fibre were, respectively, lower or similar to the matrix shear strength. These experimental results support the hypothesis of an interphase whose mechanical properties control the level of fibre-matrix stress transfer. In our fibre-matrix system the presence of the sizing leads to an interphase with lower thermomechanical stability.

The better thermomechanical stability of the interphase obtained with desized fibre was also verified by means of dynamic mechanical thermal analysis performed on single-bundle composites. In particular, ARD fibre composites showed a lower loss factor peak, which shifted at higher temperature with respect to the AR fibre composites. Moreover, the activation energy for the glass transition was higher for ARD fibre composites than for AR fibre composites.

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APPENDIX

Friction at the interface is due to normal stresses, which are the sum of the thermal shrinkage stress σ_t and the Poisson's shrinkage stress σ_p . Therefore the frictional shear stress τ_f is computable as⁴⁷

$$\tau_f = \mu(\sigma_t + \sigma_p) \quad (A1)$$

where μ is the coefficient of friction. In this work the stresses σ_t and σ_p have been evaluated using the model proposed by DiLandro *et al.*¹⁴, which yields the following expressions

$$\sigma_t = \frac{-E_{tf}E_m\Delta T[\nu_{af}(\alpha_m - \alpha_{af}) + \alpha_m - \alpha_{tf}]}{2\nu_{af}^2E_m + E_m(\nu_{tf} - 1) - E_{tf}(\nu_m + 1)} \quad (A2)$$

and

$$\sigma_p = \frac{-E_{tf}(\nu_{af} - \nu_m)\sigma_a}{2\nu_{af}^2E_m + E_m(\nu_{tf} - 1) - E_{tf}(\nu_m + 1)} \quad (A3)$$

where E is the Young's modulus, ν is the Poisson coefficient, α is the linear thermal expansion coefficient, ΔT is the difference between the matrix T_g and the actual temperature, and σ_a is the external stress applied to the matrix. The subscripts a and t refer to axial and transverse properties, while m and f refer to the matrix

and to the fibre, respectively. E_m and σ_a have been measured (see Experimental section) as a function of temperature, while the remaining parameters involved in equations (A2) and (A3) have been considered to be constant over the entire temperature range. In particular, the following values have been used: $E_{tf} = 8 \text{ GPa}$, $\alpha_m = 55 \times 10^{-6} \text{ K}^{-1}$, $\alpha_{af} = -1 \times 10^{-6} \text{ K}^{-1}$, $\alpha_{tf} = 7 \times$

10^{-6} K^{-1} , $\nu_m = 0.35$, $\nu_{af} = 0.20$, $\nu_{tf} = 0.35$. The α_m , ν_m and ν_{af} data have been taken from fibre and resin data sheets, and the other values from ref. 48. According to Rao and Drzal⁴⁹ the frictional coefficient was fixed equal to 0.6. The maximum stress applied to the sample during the fragmentation test was considered equal to the matrix tensile strength σ_m .