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 sized fibre interphase. Copyright © 1996 Elsevier Science Limited

(Keywords: interphase; fragmentation test; temperature; dynamic mechanical thermal properties)

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 methods have been developed to characterize the fibre–matrix interactions and a lot of work, both theoretical and experimental, 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 strengths, the longitudinal and transverse tensile and flexural strengths, the longitudinal compressive strength and the mode II fracture toughness. 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 absorption. However, by optimization of the physical and mechanical properties of the fibre–matrix interface, both high strength and high toughness characteristics can be achieved simultaneously. Of course, this task can be achieved 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 test and the pull-out test. 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 matrix, while others found that the interphase thermomechanical stability was lower or equal to that of the bulk resin. Some efforts to obtain more information about the thermal behaviour of the interphase have even been done using dynamic
mechanical thermal analysis$^{26-32}$ (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 Besfight 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 solvent$^{36}$. 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 $7.0 \pm 0.7 \mu m$.

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 2h, followed by 2h 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 $\sim 5 g$, 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 ($h\nu = 1253.3 eV$). 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 model$^{38}$, the mean strength as a function of fibre length $\sigma_b(L)$ is given by

$$\sigma_b(L) = \alpha L^{-1/\beta} \times \Gamma \left(1 + \frac{1}{\beta}\right)$$

(1)

where $\alpha$ and $\beta$ are the Weibull scale and shape parameters, respectively, $L$ is the fibre length and $\Gamma$ is the gamma function. The plot $\ln[\sigma_b(L)]$ versus $\ln(L)$ produced a straight line whose gradient was $-1/\beta$ and whose intercept was

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

(2)

which allowed us to evaluate $\alpha$. The applicability of the two-parameter Weibull analysis to carbon fibre is well demonstrated in the literature$^{39}$.

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 $\tau_m$ may be estimated$^{40,41}$ from the matrix tensile strength $\sigma_m$ 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...
controlled, has a precision of ±1 μg and a variable immersion speed (range 2–256 μm 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 tension. 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 equations. 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 V s⁻¹ for a few minutes. A speed of 21 μm 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 ± 0.1°C, respectively. At least five specimens have been tested for each experimental situation.

**Interfacial shear stress transfer level**

The interfacial shear stress transfer level (τ) has been evaluated through the fragmentation test and following the simplified physical model proposed by Kelly and Tyson, which yields the well known expression

\[ \langle \tau \rangle = \frac{d \sigma_c (L_c)}{2L_e} \]  

where \( d \) is the fibre diameter, \( L_c \) the critical length and \( \sigma_c (L_c) \) is the mean fibre strength at the fibre critical length. The critical length was taken to be equal to 4.3 \( L_c \), where \( L_c \) 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 test, 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 mm × 4 mm × 1 mm) of bulk matrix and on strips (15 mm × 2.5 mm × 0.8 mm) of single-bundle composite (SBC) specimens prepared as follows. A fibre bundle ~200 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 \( \Delta E \) for the glass transition has been calculated, as reported by other authors, using the following Arrhenius equation

\[ \omega = A \exp(-\Delta E/RT_g) \]  

where \( \omega \) 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 \( \Delta E \) to be calculated from the equation

\[ \ln \omega = \ln A - \Delta E/RT_g \]

**RESULTS AND DISCUSSION**

From the thermal decomposition method, the amount of sizing on the AR fibres was found to be equal to 1.41 ± 0.9 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 mm. The solvent desizing procedure caused a weight loss equal to 1.58 ± 0.03 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 literature 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>
<thead>
<tr>
<th>Table 1</th>
<th>X.p.s. analysis of as received (AR) and desized (ARD) Besfight HTA-7.3000 carbon fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre</td>
<td>O (at%)</td>
</tr>
<tr>
<td>AR</td>
<td>20</td>
</tr>
<tr>
<td>ARD</td>
<td>16</td>
</tr>
</tbody>
</table>

1069
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.

Table 2: Advancing ($\theta_{\text{adv}}$) and receding ($\theta_{\text{rec}}$) contact angles measured in water and in methylene iodide

<table>
<thead>
<tr>
<th>Material</th>
<th>$\theta_{\text{adv}}$</th>
<th>$\theta_{\text{rec}}$</th>
<th>$\theta_{\text{adv}}$</th>
<th>$\theta_{\text{rec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>84 ± 2</td>
<td>47 ± 5</td>
<td>45 ± 1</td>
<td>0</td>
</tr>
<tr>
<td>AR fibre</td>
<td>64 ± 3</td>
<td>50 ± 6</td>
<td>40 ± 1</td>
<td>24 ± 4</td>
</tr>
<tr>
<td>ARD fibre</td>
<td>60 ± 3</td>
<td>49 ± 3</td>
<td>34 ± 2</td>
<td>24 ± 4</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma$</th>
<th>$\gamma^d$</th>
<th>$\gamma^p$</th>
<th>$\gamma$</th>
<th>$\gamma^d$</th>
<th>$\gamma^p$</th>
<th>$\gamma$</th>
<th>$\gamma^d$</th>
<th>$\gamma^p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>41.9</td>
<td>34.5</td>
<td>7.4</td>
<td>37.2</td>
<td>34.1</td>
<td>3.1</td>
<td>41.9</td>
<td>34.5</td>
<td>7.4</td>
</tr>
<tr>
<td>AR fibre</td>
<td>52.0</td>
<td>36.0</td>
<td>16.0</td>
<td>45.0</td>
<td>32.0</td>
<td>13.0</td>
<td>52.0</td>
<td>36.0</td>
<td>16.0</td>
</tr>
<tr>
<td>ARD fibre</td>
<td>56.2</td>
<td>38.6</td>
<td>17.6</td>
<td>48.5</td>
<td>34.2</td>
<td>14.3</td>
<td>56.2</td>
<td>38.6</td>
<td>17.6</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Material</th>
<th>$W$ (mJ/m$^2$)</th>
<th>$W^d$ (mJ/m$^2$)</th>
<th>$W^p$ (mJ/m$^2$)</th>
<th>$W$ (mJ/m$^2$)</th>
<th>$W^d$ (mJ/m$^2$)</th>
<th>$W^p$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR fibre/epoxy</td>
<td>90.7</td>
<td>70.5</td>
<td>20.2</td>
<td>78.8</td>
<td>66.1</td>
<td>12.7</td>
</tr>
<tr>
<td>ARD fibre/epoxy</td>
<td>93.7</td>
<td>72.9</td>
<td>20.8</td>
<td>81.6</td>
<td>68.3</td>
<td>13.3</td>
</tr>
</tbody>
</table>

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 water and methylene iodide (Table 3) were used to determine the 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.

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 $\alpha$ of the desired fibres was only slightly lower than that for the as received fibres, but the shape parameter $\beta$ was slightly higher. So, following equation (1), the mean fibre tensile strength results were practically unchanged after the desizing procedure. In previous work 16 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., 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 ($\tau$) 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 authors 18-24 we found a decrease of stress transfer level as the temperature was raised. The values of ($\tau$) 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 ($\tau$) values for sized fibres are lower than the bulk matrix shear strength, and at higher temperatures we obtained ($\tau$) values slightly higher than the shear strength of the bulk matrix (Figure 2). Moreover, for the desized fibres ($\tau$) values were equal to (up to 80°C) or greater than the shear strength of the bulk matrix. It is worth noting that
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 (\tau), 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 principle23 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>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Bulk matrix</th>
<th>Single-bundle composite with AR fibre</th>
<th>Single-bundle composite with ARD fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature at tan\delta peak (°C)</td>
<td>Tan\delta peak (°C)</td>
<td>Temperature at tan\delta peak (°C)</td>
</tr>
<tr>
<td>1</td>
<td>1.1372</td>
<td>152.8</td>
<td>1.0803</td>
</tr>
<tr>
<td>3</td>
<td>1.1148</td>
<td>156.0</td>
<td>1.0865</td>
</tr>
<tr>
<td>10</td>
<td>1.0906</td>
<td>159.0</td>
<td>1.0924</td>
</tr>
<tr>
<td>30</td>
<td>1.0705</td>
<td>162.2</td>
<td>0.943</td>
</tr>
<tr>
<td>50</td>
<td>1.0582</td>
<td>164.5</td>
<td>0.1891</td>
</tr>
</tbody>
</table>
Thermomechanical behaviour of interfacial region: A. Pegoretti et al.

![Graph](image)

**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>
<thead>
<tr>
<th>Table 6</th>
<th>Activation energies for glass transition obtained from d.m.t.a. measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Activation energy, ΔE (kJ mol⁻¹)</td>
</tr>
<tr>
<td>Bulk matrix</td>
<td>530</td>
</tr>
<tr>
<td>Single-bundle composite with AR fibre</td>
<td>424</td>
</tr>
<tr>
<td>Single-bundle composite with ARD fibre</td>
<td>527</td>
</tr>
</tbody>
</table>

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 (τ) 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 (τ) values decreased as the test temperature increased. The values of (τ) for the desized fibres were significantly higher than those obtained with the sized fibres. By comparison with bulk matrix mechanical properties, the (τ) 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 σt and the Poisson’s shrinkage stress σp. Therefore the frictional shear stress τf is computable as

\[ \tau_f = \mu (\sigma_t + \sigma_p) \]  \hspace{1cm} (A1)

where \( \mu \) is the coefficient of friction. In this work the stresses \( \sigma_t \) and \( \sigma_p \) have been evaluated using the model proposed by DiLandro et al., which yields the following expressions

\[ \sigma_t = -E_{ef}v_{ad}\Delta T\left(v_{ad}(\alpha_m - \alpha_{ad}) + \alpha_m - \alpha_{ad}\right) \]  \hspace{1cm} (A2)

and

\[ \sigma_p = -E_p(\nu_{ef} - \nu_{en})\]  \hspace{1cm} (A3)

where \( E \) is the Young’s modulus, \( \nu \) is the Poisson coefficient, \( \alpha \) is the linear thermal expansion coefficient, \( \Delta T \) is the difference between the matrix \( T_m \) and the actual temperature, and \( \sigma_e \) 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 $\sigma_t$ 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: $E_{df} = 8$ GPa, $\alpha_m = 55 \times 10^{-6}$ K$^{-1}$, $\alpha_{df} = -1 \times 10^{-6}$ K$^{-1}$, $\sigma_t = 7 \times 10^{-6}$ K$^{-1}$, $\nu_m = 0.35$, $\nu_{df} = 0.20$, $\nu_t = 0.35$. The $\alpha_m$, $\nu_m$ and $\nu_{df}$ data have been taken from fibre and resin data sheets, and the other values from ref. 48. According to Rao and Drzač 89 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 $\sigma_m$. 

1074