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EFFECT OF TEMPERATURE AND STRAIN RATE ON INTERFACIAL SHEAR STRESS TRANSFER IN CARBON/EPOXY MODEL COMPOSITES

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Abstract

The amount of stress transferred in a composite from the matrix to the fibre has been determined in an epoxy/carbon system by using a fragmentation test on single-fibre model composites (microcomposites), as a function of temperature and strain rate. Experiments, performed on microcomposites containing commercial carbon fibres, with and without sizing agent, and an epoxy resin of low glass transition temperature (T_g), indicate that the interfacial shear strength, $\langle\tau\rangle$, decreases sharply as the test temperature approaches the T_g of the constituent surrounding the fibre. Moreover, while in desized fibre composites the interfacial shear strengths compare well with the matrix shear strength, in sized fibre composites the measured $\langle\tau\rangle$ values appear to be strongly influenced by the presence of an interphase. $\langle\tau\rangle$ values measured for sized fiber microcomposites are higher than the matrix shear strength.

The contribution to adhesion of frictional stresses, exerted by the matrix on the fibre as a result of thermal and Poisson contractions, appears to be negligible with respect to the $\langle\tau\rangle$ values obtained from the fragmentation test.

Keywords: fibre/matrix adhesion, fragmentation test, interphase/matrix properties, microcomposites, stress transfer, temperature

1 INTRODUCTION

Structure and properties of the fibre/matrix interface play a major role in controlling the mechanical and physical properties of composite materials. In particular, the interfacial shear strength, $\langle\tau\rangle$, is one of the most important parameters in determining the strength and the toughness of a composite, since the load applied to the composite is transmitted from the matrix to the fibre through the interface.

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In polymeric matrix composites, among the numerous variables which affect the properties of the interface (chemical and physical bonds, mechanical interlocking, surface treatments, sizing, moisture content, etc.), temperature and strain rate are of primary importance. Properties and mechanical behaviour of a polymeric matrix, in fact, strongly depend on temperature, with dramatic changes when the temperature approaches the polymer T_g. In this temperature region, the viscoelastic nature of the material is enhanced and the polymer mechanical response becomes highly strain-rate dependent.

Aiming at predicting the fibre/matrix interface mechanical properties, many authors have investigated and discussed the relationship between interfacial properties and constituents properties, and have studied the role played by matrix[1,2,3] and interphase[1–6] properties, as well as surface treatments.[4,7–10] Nevertheless in epoxy/carbon composites the dependence of $\langle\tau\rangle$ from constituents properties is not completely understood, and we are still far from being able to predict the interfacial shear stress transfer from matrix, fibre, and interphase behaviour. In particular, from experimental studies on carbon/epoxy or glass/epoxy composites, it appears that in high T_g resin systems the $\langle\tau\rangle$ values are near or somewhat below the shear strength of the bulk matrix,[9] whereas in low T_g resin systems $\langle\tau\rangle$ can be considerably higher than the matrix shear strength.[2,7]

The aim of this study was, first, to evaluate the effect of temperature and strain rate on $\langle\tau\rangle$ in a low T_g epoxy/carbon composite, and, secondly, to investigate the cause of the encountered behaviour, focussing, in particular, on the relationship between $\langle\tau\rangle$ and the matrix and interphase properties.

2 THEORY

The interfacial strength, $\langle\tau\rangle$, has been evaluated through the fragmentation test and following the simplified physical model proposed by Kelly and

Tyson,[11] which yields the well-known expression:

$$\langle\tau\rangle = \frac{d\bar{\sigma}_{f_b(L_c)}}{2L_c} \quad (1)$$

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. According to Kelly and Tyson, 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 fibre strength has been computed according to the Weibull theory:[12]

$$\bar{\sigma}_{f_b(L)} = \alpha L^{-1/\beta}\Gamma\left(1+\frac{1}{\beta}\right) \quad (2)$$

in which $\bar{\sigma}_{f_b(L)}$ is the mean fibre strength, L the length of the fibre, Γ the Gamma function, and α and β are the Weibull scale and shape parameters, respectively.

When investigating how interfacial properties relate to the matrix, fibre and interphase properties, it is worth remembering that $\langle\tau\rangle$ values obtained from fragmentation tests are sensitive to the interfacial bond shear strength, τ_s, as well as to the frictional shear strength, τ_f, and hence:

$$\langle\tau\rangle = f(\tau_s, \tau_f) \quad (3)$$

Friction at the interface is due to normal stresses, which are the sum of the cure shrinkage stress, σ_c, and the normal compressive stress arising from Poisson contraction, σ_p. The frictional term is therefore computable as:[13,14]

$$\tau_f = \mu(\sigma_c + \sigma_p) \quad (4)$$

where μ is the coefficient of friction. In this work the stresses σ_c and σ_p have been evaluated by using the model developed by DiLandro & Pegoraro,[15] which yields the following expressions:

$$\sigma_c = \frac{-E_{tf}E_m\Delta T[\nu_{af}(\alpha_m - \alpha_{af}) + \alpha_m - \alpha_{tf}]}{2\nu_{af}^2E_m + E_m(\nu_{tf}-1) - E_{tf}(\nu_m+1)} \quad (5)$$

and,

$$\sigma_p = \frac{-E_{tf}(\nu_{af} - \nu_m)\sigma_a}{2\nu_{af}^2E_m + E_m(\nu_{tf}-1) - E_{tf}(\nu_m+1)} \quad (6)$$

where E is the Young's modulus, ν is the Poisson ratio, α is the linear thermal expansion coefficient, ΔT the difference between the matrix T_g and the test 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. The interfacial shear bond strength, that is the maximum shear stress born by the interface in absence of frictional stresses, is directly related to chemical and physical bonds, mechanical interlocking and surface treatments. In this respect it should be clear that, for composites with an interphase between fibre and matrix, it is possible to distinguish two different interfaces and, hence, in order to study the mechanism that limits the transfer of shear stress between fibre and matrix, it is of primary importance to identify if the failure takes place at the fibre/interphase interface or at the interphase/matrix interface.

3 EXPERIMENTAL

3.1 Materials

The fibre used in this work was Besfight HTA-7-3000 (TOHO), a high strength carbon fibre manufactured from PAN precursor. The fibres were surface treated and sized by the manufacturer with an epoxy compatible sizing. For the purpose of this study some fibres were desized (washed for two hours in boiling chloroform and then vacuum degassed); throughout this paper the as-received fibres (and their composites) will be identified as BF while desized fibres (and their composites) will be identified as BFD.

The matrix resin used was Henkel CHEM RES E 95, a low-density epoxy resin from Bisphenol-A, which was cured by 50 wt% of an epoxy amido-amidic hardener, Henkel REAMMIDE PGF 24. The resin was cured for two hours at 90°C and then slowly cooled overnight.

3.2 Fibre properties

From observations performed with a scanning electron microscope (Cambridge Stereoscan 200) the fibres appeared to have an almost circular cross-section. The diameters of the fibres were measured by using an optical microscope and an image analyser system (Fig. 1). More than 50 specimens were measured, giving an average diameter equal to $7 \pm 0{\cdot}7\ \mu$m. The Young's modulus, E, of single fibres was evaluated in accordance with the ASTM D 3379-75 standards by using an Instron 4502 tensile tester, at a cross-head speed of 0.2 mm min^{-1} and at a test temperature of 20°C. From the tests (about 60 specimens) performed on samples with gauge lengths ranging from 5·2 mm to 20·8 mm we obtained an E value of 246 ± 26 GPa.

The fibre strength was evaluated by two different methods, by the single-fibre test (SFT) and by continuous monitoring of the fragmentation test (CMFT). In the SFT the strengths of single fibres were measured according to the ASTM D 3379-75 standard using an Instron 4502 machine, at a cross-head speed of 0·2 mm min^{-1} and at a temperature of 20°C. At least 15 specimens were tested at each sample gauge length (5·2, 9·9, 14·8, 20·8 mm). As a result we found that the distribution of fibre strength conformed well to a Weibull model at each gauge length, but the value of the shape parameter was not constant in the four specimens. For that reason the strength of the fibres was estimated from the Weibull parameters (α, β)

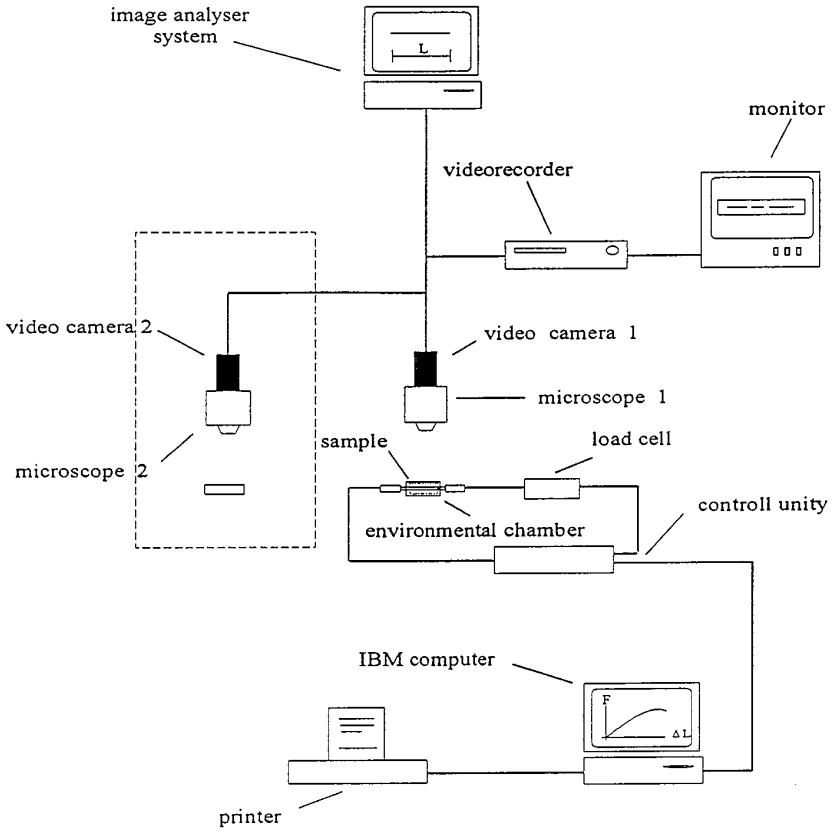

Fig. 1. Schematic illustration of the fragmentation test apparatus.

determined from an the interpolation of raw data based on eqn (2) in which L was the gauge length.[16]

In the CMFT the fibre strength was measured according to the procedure presented by Yavin *et al.*[17] and using the custom-made apparatus for fragmentation testing shown in Fig. 1. The apparatus consists of a small tensile tester (Minimat, by Polymer Laboratories), equipped with an environmental thermostatic chamber, and placed under an optical stereomicroscope (Leica-Wild M3Z). From the microscope, the image of the sample is sent, through a video-camera, to a video-recorder and then to a personal computer with image analysis software (Met1 by Pertel). Single-fibre composite sample preparation is described later (see interfacial shear strength). Three samples were tested at a cross-head speed of $0{\cdot}2\,\text{mm}\,\text{min}^{-1}$ and at a temperature of 20°C and for each sample the whole fragmentation process was recorded and then analysed, in order to obtain the mean fragment length at different fibre stress levels. According to Yavin *et al.*,[7] by supposing the same deformation in the fiber and in the composite, the link between the stress σ_a applied to the sample (which we measure during the test) and the fibre stress σ_f is assumed here to be given by $\sigma_f = (E_f/E_m)\sigma_a$ (where E_f and E_m are the fibre and matrix moduli respectively). Of course, at each fibre break σ_f is equal to the fibre strength $\bar{\sigma}_{f_b}$. A plot of $\ln(\bar{L})$, where $\bar{L}$ is the mean fragment length, against $\ln(\bar{\sigma}_{f_b})$ yields a straight line with slope equal to the Weibull shape parameter β. The Weibull scale parameter, α, can be calculated from the value of the intercept. The results of SFT and CMFT, listed in Table 1, show good agreement between the two methods. Nevertheless, since CMFT measures the strengths of fibres at gauge lengths closer to the critical length than the SFT, we decided to calculate the fibre strength by means of the Weibull parameters obtained from CMFT.

Table 1. Weibull parameters of the Besfight fibres evaluated by using the single-fibre test (SFT) and continuous monitoring of fragmentation test (CMFT)

Method	α (GPa) (scale parameter)	β (shape parameter)
SFT	5·949	4·8
CMFT	5·482	5·0

3.3 Matrix properties

The glass transition temperature of the resin was evaluated by using a differential scanning calorimeter (Mettler DSC 30). Scans were run from −50 to +250°C, at a heating rate of $10°\text{C}\,\text{min}^{-1}$, under a nitrogen flux of $10\,\text{ml}\,\text{min}^{-1}$. The T_g of the cured resin,

Table 2. Mechanical properties of the epoxy matrix at various temperatures and strain rates

Temperature (°C) (strain rate = 0·008 min^{-1})	E_m (MPa)	Standard deviation (MPa)	σ_m (MPa)	Standard deviation (MPa)
10	1253	106	28·9	3·9
20	882	78	13·4	3·3
30	468	52	15·1	3·0
40	202	26	6·1	1·8
50	50	8	1·0	0·3
Strain rate (min^{-1}) (temperature = 20°C)	**E_m (MPa)**	**Standard deviation (MPa)**	**σ_m (MPa)**	**Standard deviation (MPa)**
0·002	750	55	12·0	2·0
0·004	785	59	12·1	2·3
0·008	882	78	13·4	3·3
0·016	1150	102	22·3	4·5

calculated at the inflection point of the energy versus temperature curve, is 39°C. Mechanical properties were evaluated by means of an Instron 4502 tensile tester equipped with a temperature-controlled chamber. Five specimens were tested at each temperature. Test specimens, consisting of strips of uniform width and thickness (average dimensions of 50 mm × 3·5 mm × 0·7 mm) with a gauge length of 25 mm, were cut from a resin sheet cured at 90°C for two hours. Tests were performed at different strain rates ranging from 0·002 to 0·016 min^{-1} at a temperature of 20°C, and at temperatures varying from 10 to 50°C at a fixed strain rate of 0·008 min^{-1}. The matrix shear strength, τ_m, was estimated from the matrix tensile strength through the von Mises relationship, $\tau_m = \sigma_m/\sqrt{3}$, in which σ_m is the matrix tensile strength.[10] Mechanical properties of the matrix, that is elastic modulus, E_m, tensile strength, σ_m, and shear strength, τ_m, are listed in Table 2 for various temperatures and strain rates.

3.4 Interfacial shear strength

The interfacial shear strength was evaluated from fragmentation tests performed with the apparatus already described (Fig. 1). Single-fibre composite samples were prepared according to the following procedure: (i) a mould was obtained from a polyethylene sheet (150 mm × 100 mm × 1 mm) on which two strips of adhesive tape were placed at a distance of 50 mm; (ii) 10–15 fibres (~80 mm long) were carefully separated from the fibre tow, mounted on the mould and held in place by the fixing of their ends on the tape with a small amount of cyanoacrylate glue; (iii) two more strips of tape were imposed on the fibre ends, in order to prevent any leakage of resin during the cure; (iv) the mould was vacuum degassed; (v) after mixing, the liquid resin was vacuum degassed and then poured into the mould; (vi) the assembly was transferred to an oven where the resin was cured (two hours at 90°C); (vii) after cooling down to room temperature the laminae of fibres and resin were detached from the mould and single-fibre composite samples (50 mm × 5 mm × 0·3 mm) were cut by using a specially designed cutter. At least three samples with a gauge length of 25 mm were tested at each temperature and strain rate condition, up to a strain of about 10%, in order to reach the whole saturation of the fragmentation process. Segment lengths were measured via the optical microscope and the image analysis system.

3.5 Failure morphology

A Leitz Ortholux II POL-BK (transmitted light) microscope, equipped with a light polarizer, was employed to observe the photoelastic response of the resin matrix at the interface during the test and the fibre fracture propagation, both in BF and in BFD samples.

4 RESULTS AND DISCUSSION

4.1 Effect of temperature on $\langle\tau\rangle$

Fragmentation tests were conducted from 10 to 50°C (strain rate of 0·008 min^{-1}) in order to investigate how temperature affects the transfer of shear stress at the interface. Although some experiments were performed at 0°C, we did not obtain $\langle\tau\rangle$ measurements, because at this temperature the epoxy resin was too brittle and premature matrix failure prevented fibre fragmentation. This result is not surprising since, as predicted by an empirical law,[18] to obtain fragmentation the matrix strain at break must be at least three times greater than the strain at break of the fibre, and at 0°C this condition was not satisfied.

The experimental relationship between $\langle\tau\rangle$ and test

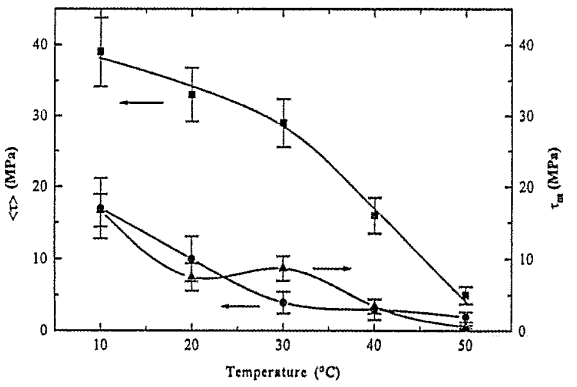

Fig. 2. Effect of temperature on interfacial shear strength values in BF (■) and BFD (●) single fibre composites and on the matrix shear strength (▲).

temperature is given in Fig. 2. In the same figure, the matrix shear strength versus temperature has been also plotted.

For both BF and BFD fibre composites, $\langle\tau\rangle$ decreases as temperature increases, with values that remain significantly higher for the BF composites and reach a level plateau for BFD composites, beginning at around 30°C. Matrix shear strengths superimpose quite well on the interfacial shear strength of desized fibre composites, implying that, in this case, fibre/matrix adhesion mainly depends on the bulk matrix properties, with a strong decrease in correspondence of matrix T_g.

The $\langle\tau\rangle$ values for BF composites are much higher than the bulk matrix shear strength. This difference is not completely understood yet but the existence of an interphase surrounding the fibre more thermo-mechanically stable than the matrix can be supposed. A knee at about 30°C separates the curve into two parts with different slopes, the first of which is similar to the slope of the first part of the BFD curve.

As suggested by some authors, and in particular by Drzal,[5] the size interphase is an epoxy rich layer (≈200 nm) which is usually stiff and brittle. Recently it has been however reported[22] that the composition of an epoxy resin could be affected by the presence of the fibre, which absorbs part of the curing amine on its surface, so causing a stoichiometric imbalance of the epoxy resin in proximity of the fibre. Amounts of curing amine smaller or larger than the stoichiometric one, lead to lower crosslinking density and, therefore, to lower resin T_g. In a recent paper, Skourlis and McCullough[23] have found that the glass transition temperature of a sizing epoxy resin drops from about 160°C to about 60°C, if the resin is cured with the assumed stoichiometry imbalance of the interphase region.

By contrast, DiBenedetto and Lex,[7] working on glass fibres in an epoxy resin matrix cured with amine amounts larger than stoichiometric, have measured a considerable increase in the bulk resin T_g, also attributed to the adsorption of the polyamine hardener on the fibre surface. In this case, the increase in matrix T_g in the composite was considered to be one of the factors accounting for the significantly larger interfacial shear strength measured with respect to the shear strength of the pure epoxy matrix.

The behaviour reported in Fig. 2 for BF composites could be explained by assuming predominant effects of matrix or sizing agent behaviour on the interfacial shear strength, depending on temperature, and associated with modifications occurring in the matrix or in the interphase layer. For temperatures higher than 30°C the matrix reaches an almost constant shear strength, but $\langle\tau\rangle$ values continue to decrease, so indicating an interphase glass transition temperature presumably higher than that of the bulk matrix. The previous explanation assumes that, in the case investigated, adhesion is predominantly controlled by the strengths of the bulk matrix and interphase resins. A study directed to a better understanding of the phenomenon is in progress.

4.2 Effect of strain rate on $\langle\tau\rangle$

The sensitivity to strain rate of the interfacial properties in our low-T_g epoxy resin composites was evaluated by measuring the $\langle\tau\rangle$ value at four different strain rates ranging from 0·002 min^{-1} to 0·016 min^{-1} at a constant temperature of 20°C. We were unable to widen the range of study beyond 0·016 min^{-1} because in that condition the matrix was too brittle and the saturation of the fragmentation process was not reached. The experimental results (Fig. 3) show that the measured interfacial shear stress transmission is strongly affected by the rate at which the load is applied to the material.

For both composites, the higher the applied strain rate the higher the $\langle\tau\rangle$ value. Moreover BF samples $\langle\tau\rangle$ values are always higher (2–3 times) than those of BFD samples. The data of fragmentation tests have been compared with the values of matrix shear strength and the results (Fig. 3) indicate that $\langle\tau\rangle$ values of BFD samples compare quite well with shear strength of the bulk matrix in the whole experimental range.

4.3 Failure modes

From polarised light microscope observations performed on samples during the fragmentation test, it has been found that BF and BFD composites exhibited two distinct mechanisms which present some

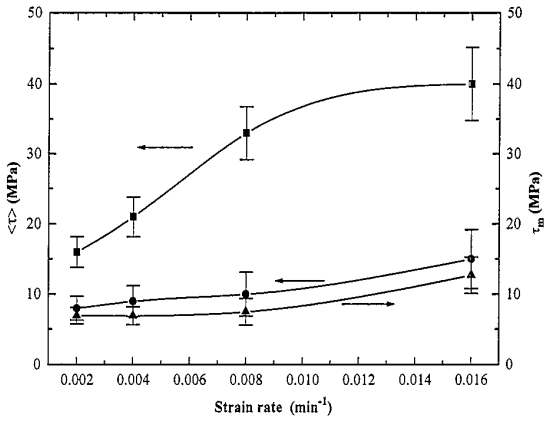

Fig. 3. Effect of strain rate on interfacial shear strength values in BF (■) and BFD (●) single fibre composites and on the matrix shear strength (▲).

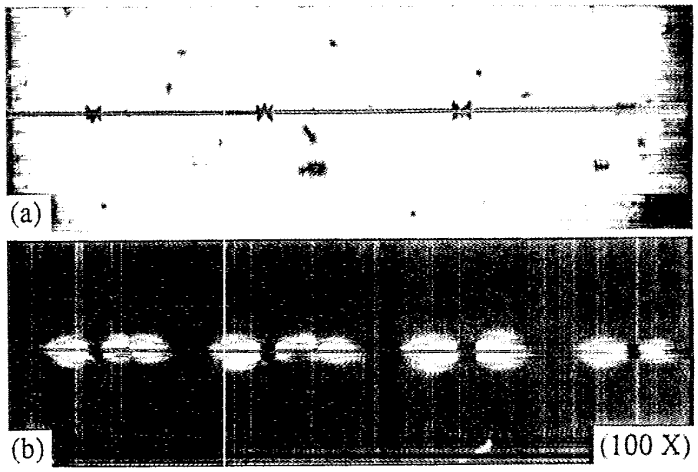

Fig. 4. Optical microscope micrographs (100×) of a BF microcomposite during the fragmentation process: matrix failure observed with (a) not-polarized transmitted light, (b) polarized transmitted light.

common characteristics regardless of the experimental conditions. In BF composites (Fig. 4) a crack starts to grow near the fibre break (disk-shape) and then enlarges advancing through the interphase and the matrix, perpendicularly to the fibre axis (butterfly shape); the fibre/interphase interface is subjected to increasing stresses, inducing yielding in interphase resin (and matrix), as indicated by permanent birefringence patterns around the fibre after releasing the load. In BFD composites (Fig. 5) the crack starts to grow, once again, close to the fibre break points, but then the crack area running along the fibre/matrix interface increases (debonding), without developing large and persistent birefringence patterns. The debonding process slows down and stops when the saturation of fragmentation is reached. As pointed out by many authors,[7,9] this mechanism suggests that the interface of BF composites is 'strong' (i.e. high interfacial shear strength), whereas the interface of BFD composites is 'weak' (i.e. low interfacial shear strength). These results accord well with the numerical data obtained from fragmentation tests.

4.4 Evaluation of the frictional shear strength

In order to study the nature of $\langle\tau\rangle$ it is fundamental to distinguish the role of the frictional stresses. The frictional shear strength was estimated by eqn (4), where the frictional coefficient was fixed to 0.6, according to the results obtained by Rao and Drzal[2] for carbon/epoxy systems. The values of the cure shrinkage stress, σ_c, and the Poisson contraction stress, σ_p, were computed [eqns (5) and (6)] from the data listed in Table 3, ΔT being equal to the difference between the matrix glass transition temperature and the test temperature. The maximum stress applied to the sample during the fragmentation test was considered equal to the matrix tensile

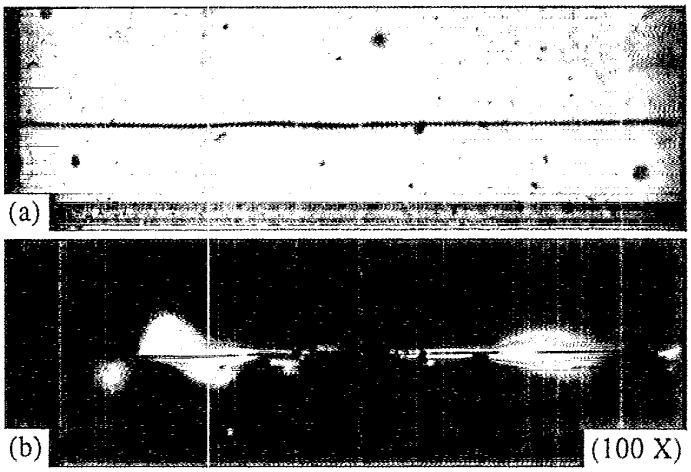

Fig. 5. Optical microscope micrographs (100×) of a BFD microcomposite during the fragmentation process: interface debonding observed with (a) not-polarized transmitted light, (b) polarized transmitted light.

Table 3. Properties of the matrix and the fibre used for the frictional shear strength evaluation (data are taken from fibre and resin data sheets and (*) from Ref. 21)

Property	Value
E_{tf} (GPa)	8*
α_m (10^{-6} K^{-1})	55
α_{af} (10^{-6} K^{-1})	−1*
α_{tf} (10^{-6} K^{-1})	7*
ν_m	0·35
ν_{af}	0·20
ν_{tf}	0·20*

Table 4. Cure shrinkage stress, σ_c, normal compressive stress, σ_p, and frictional shear strength, τ_f, at the interface (frictional coefficient = 0·6) at various temperatures and strain rates

Temperature (°C) (strain rate = 0·008 min^{-1})	σ_c (MPa)	σ_p (MPa)	τ_f (MPa)
10	1·52	2·97	2·69
20	0·73	1·36	2·09
30	0·20	1·62	1·09
40	0·00	0·66	0·40
50	—	0·11	0·07
Strain rate (min^{-1}) (temperature = 20°C)	**σ_c (MPa)**	**σ_p (MPa)**	**τ_f (MPa)**
0·002	0·63	1·27	1·14
0·004	0·65	1·27	1·15
0·008	0·73	1·36	1·25
0·016	0·94	2·27	1·93

strength, σ_m (Table 2). With regards to BF composites, it should be pointed out that the model referred to[15] is no longer satisfactory, since it does not consider the interphase between fibre and matrix. Nevertheless, owing to the lack of simple three-component models, we have used the DiLandro and Pegoraro model so as to have an estimate of the frictional stresses, keeping in mind however that for BF samples the results are likely to be slightly below the actual values.

From the results listed in Table 4, it is evident that the frictional shear stress decreases as the test temperature increases and as the strain rate decreases, even if both for BF and BFD composites the frictional shear stresses are very small with respect to $\langle\tau\rangle$ values. Furthermore, it can be seen that Poisson contraction plays the larger effect, consistently with the low ΔT of the matrix.

5 CONCLUSIONS

In this work the interfacial shear strength in composites with carbon fibres and a low-T_g epoxy matrix has been studied by using the fragmentation test. From the experimental data, it appears that the interfacial shear strength falls rapidly as the temperature approaches the T_g of the constituent surrounding the fibre. The presence of a sizing agent improves the fibre/matrix adhesion, to a level higher than the matrix shear strength. In BF composites the thin size coating is responsible for the higher values of $\langle\tau\rangle$; unfortunately without data for the shear strength of this component it is not possible to determine exactly whether this better interfacial strength is primarily due to the presence of a stiff interphase (modulus and thickness effect) which modifies the stress field around the fibre[6] or to the higher strength of the interphase.

Owing to the strong viscoelastic characteristics of the matrix at the investigated temperature, the interfacial shear strengths are strongly dependent on the strain rate. In particular $\langle\tau\rangle$ is found to increase as strain rate increases.

The comparison between sized and desized fibre composites shows that the presence of a thermo-mechanical resistant interphase modifies the mechanism of failure from matrix failure (sized fibres) to interfacial debonding (desized fibres).

An estimation of thermal and Poisson contractions reveal that frictional stress contributions are very small when compared with the measured interfacial shear strength.

REFERENCES

1. Daadbin, A., Gamble, A. J. & Sumner, N. D., The effect of the interphase and material properties on load transfer in fibre composite. *Composites,* **23**(4) (1992) 210–214.
2. Rao, V. & Drzal, L. T., The dependence of interfacial shear strength on matrix and interphase properties. *Polym. Comp.,* **12**(1) (1991) 48–56.
3. Asloun, El. M., Nardin, M. & Schultz, J., Stress transfer in single-fiber composites: effect of adhesion, elastic modulus of fibre and matrix, and polymer chain mobility. *J. Mater. Sci.,* **24** (1989) 1835–1844.
4. Wu, H. F., Biresaw, G. & Laemmle, J. T., Effect of surfactant treatments on interfacial adhesion in single graphite/epoxy composites. *Polym. Comp.,* **12**(4) (1991) 281–288.
5. Drzal, L. T., The interphase in epoxy composites. In *Advances in Polymer Science, 75: Epoxy Resins and Composites II,* ed. K. Dusek. Springer Verlag, Berlin, 1985, pp. 1–32.
6. DiAnselmo, A., Accorsi, M. L. & DiBenedetto, A. T., The effect of an interphase on the stress and energy distribution in the embedded single fibre test. *Comp. Sci. Tech.,* **44** (1992) 215–225.
7. DiBenedetto, A. T. & Lex, P. J., Evaluation of surface treatments for glass fibers in composite materials. *Polym. Engng Sci.,* **29**(8) (1989) 543–555.
8. Drzal, L. T., Rich, M. J. & Lloyd, P. F., Adhesion of graphite fiber to epoxy matrices: I. role of fiber surface treatment. *J. Adhesion,* **16** (1982) 1–30.

9. DiBenedetto, A. T., Measurement of thermomechanical stability of interphases by the embedded single fiber test. *Comp. Sci. Tech.*, **42** (1991) 103–123.
10. Harris, B., Braddell, O. G., Lefebvre, C. & Verbist, J., The surface treatment of carbon fibres by electro-polymerisation and plasma polymerisation. *Plastic Rubber Compos. Proc. Appl.*, **18** (1992) 221–240.
11. Kelly, A. & Tyson, W. R., Tensile properties of fibre-reinforced metals: copper/tungsten and copper/molybdenum. *J. Mech. Phys. Solids*, **13** (1965) 329–350.
12. Weibull, W., A statistical distribution function of wide applicability. *J. Appl. Mech.*, **18** (1951) 293–296.
13. Piggott, M. R., Debonding and friction at fibre–polymer interfaces. I: Criteria for failure and sliding. *Comp. Sci. Tech.*, **30** (1987) 295–306.
14. Lacroix, Th., Tilmans, B., Keunings, R., Desaeger, M. & Verpoest, I., Modelling of critical fibre length and interfacial debonding in the fragmentation testing of polymer composites. *Comp. Sci. Tech.*, **43** (1992) 379–387.
15. DiLandro, L. & Pegoraro, M., Thermal stresses and adhesion in carbon fibre/thermoplastic matrix system. In *Interfacial Phenomena in Composites Materials '91*, ed. I. Verpoest and F. Joens. Butterworths, London, 1991.
16. Asloun, El. M., Donnet, J. B., Guilpain, G., Nardin, M. & Schultz, J., On the estimation of tensile strength of carbon fibre at short lengths. *J. Mater. Sci.*, **24** (1989) 3504–3510.
17. Yavin, B., Gallis, H. E., Scherf, J., Eitan, A. & Wagner, H. D., Continuous monitoring of the fragmentation phenomenon in single fiber composite materials. *Polym. Comp.*, **12**(6) (1991) 436–446.
18. Herrera-Franco, P. J. & Drzal, L. T., Comparison of methods for the measurement of fibre/matrix adhesion in composites. *Composites*, **23**(1) (1992) 2–27.
19. Bascom, W. D. & Jensen, R. M., Stress transfer in single fiber/resin tensile tests. *J. Adhesion*, **19** (1986) 219–239.
20. Brahatheeswaran, C. & Gupta, V. B., Internal stress in a cured epoxy resin system. *Polymer*, **34**(2) (1993) 289–294.
21. Riggs, D. M., Shuford, R. J. & Lewis, R. W., Graphite fibers and composites. In *Handbook of Composites*, ed. G. Lubin. Van Nostrand Reinhold, New York, 1982, pp. 196–271.
22. Palmese, G. R. & McCullough, R. L., Effect of epoxy-amine stoichiometry on cured resin material properties. *J. Appl. Polym. Sci.*, **46** (1992) 1863–1873.
23. Skourlis, T. P. & McCullough, R. L., The effect of temperature on the behaviour of the interphase in polymeric composites. *Comp. Sci. Tech.*, **49** (1993) 363–368.