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Interfacial effects in carbon–epoxies

Part 3 *Toughness with short fibres*

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The work of fracture has been measured, using the Izod test, for short-fibre laminates. The fibres were 2 mm long and in one series of experiments were aligned, and in a second series of experiments they were random in the plane of the laminate. The work of fracture increased monotonically with increasing fibre content and fibre critical length, but values were less than expected on the basis of established fibre pull-out theory. The low values were probably due to the high resistance to debonding of these composites, since the fibre pull-out lengths at the fracture surfaces were very much smaller than the fibre critical lengths.

1. Introduction

Carbon-fibre composites, while having good specific strengths and Young's moduli, are notorious for their lack of toughness. Various methods have been proposed for improving the toughness; the method currently used is hybridization with glass or Kevlar fibres [1–3], but this causes losses in other properties. Impairing the fibre–matrix bond gives a large improvement in toughness, but causes a loss in shear strength [4]. The use of fibre bundles can give improvements of more than an order of magnitude [5], but though perhaps applicable to filament-wound structures, this is impractical for laminates. Control of matrix shrinkage pressure [6] has so far yielded increases of about 100% [7].

In the case of short-fibre composites, the fibre aspect ratio has an important effect [8]. However, short-fibre composites have not been investigated in a systematic fashion. This paper reports results on tests with composites made with fibres surface treated in various ways, so that the fibre critical lengths were varied.

2. Experimental methods

Union Carbide pitch precursor P55S fibres were used in this work. They were cut to 2 mm lengths, and as received were sized. Before use, some were de-sized, others were de-sized and then etched with 70% nitric acid for 6 h, and still others were coated with silicone oil (Dow Corning 200). The critical lengths of these fibres were measured as described previously [9].

The resin matrix was Shell Epon 815, with 19% Ancamine 1482 added as hardener. The resin was cured at 100° C, and then post-cured at 160° C for 4 h.

The aligned fibre composites were made as described in the first paper in this series [9] and the random fibre composites as described in the second paper [10].

Testing was carried out on a Tinius Olsen Plastic Impact Tester, using the Izod test. The specimens were 65 mm long, 13.5 ± 0.5 mm wide, with a notch 1.5 ± 0.5 mm deep, cut at the midpoint of the length. The thickness depended on fibre volume fraction (V_f) and was 3.5 ± 1.5 mm.

Fractography was carried out using a scanning electron microscope.

3. Results

The work of fracture estimated from the Izod test was not a linear function of fibre volume fraction, either for aligned fibres (Fig. 1) or for random fibres (Fig. 2) over the range of volume fractions tested.

In the case of the aligned fibres, the coated fibres gave the highest work of fracture, G_i, while the other fibres gave results which were about 15% lower. The values at $V_f = 0$, 0.15 and 0.2 fitted an expression of the form

$$G_i = V_f G_{fi} + V_m G_m \qquad (1)$$

where G_m is the work of fracture of the matrix ($0.2\,kJ\,m^{-2}$), and G_{fi} represents the work contributed by the fibres and the fibre–matrix interfacial region. G_{fi} has values of about $20\,kJ\,m^{-2}$ for the coated fibres and $17\,kJ\,m^{-2}$ for the sized, de-sized and etched fibres. For $V_f > 0.2$ the work of fracture was less than that given by Equation 1, but still increased linearly with increasing V_f.

When random fibres were used (Fig. 2) the results fitted Equation 1 for $V_f = 0$, 0.15 and 0.2 for all but the coated fibres. This time G_{fi} came to $32\,kJ\,m^{-2}$ for the sized and etched fibres and $37\,kJ\,m^{-2}$ for the de-sized fibres. For $V_f = 0.25$ the work of fracture was less than that given by Equation 1, but, as for the aligned fibres, still increased linearly with V_f. The coated fibres gave composites which had works of fracture which increased monotonically but not linearly with increasing V_f. The slope of the line joining the results at $V_f = 0$ and $V_f = 0.15$ is equivalent to $G_{fi} = 75\,kJ\,m^{-2}$.

Micrographs of the fracture surfaces (Figs. 3 to 6) showed that in all cases relatively little fibre pull-out took place. Even the coated fibres only had pull-out

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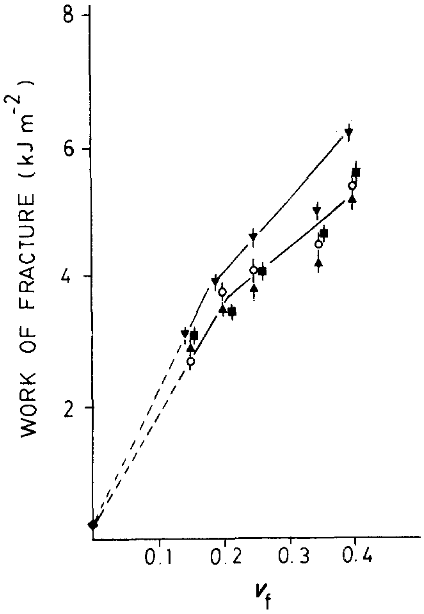

Figure 1 Work of fracture for aligned fibre composites. Fibres were 2 mm long; (▲) sized, (○) etched, (■) de-sized, (▼) silicone-coated.

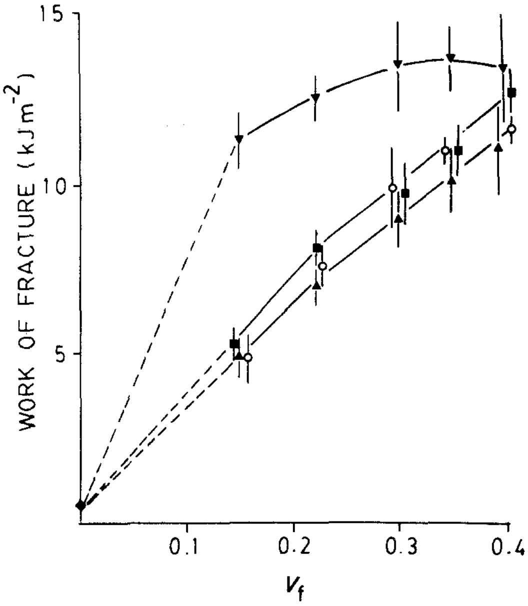

Figure 2 Work of fracture for random fibre composites. Fibres were 2 mm long; (▲) sized, (○) etched, (■) de-sized, (▼) silicone-coated.

lengths which barely exceeded twenty diameters (Figs. 5 and 6), while the sized fibres had pull-out lengths which were less than ten diameters (Figs. 3 and 4).

4. Discussion

The results do not fit current theoretical ideas. Thus, we expect the work of fracture G_1, to be a linear function of fibre volume fraction:

$$G_1 = V_f G_f^* + V_m G_m^* + G_i \tag{2}$$

where G_f^* is related to, but usually somewhat greater than, the work of fracture of the fibres. G_m^* represents the work of fracture of the matrix in the presence of fibres, and can be very much less than the corresponding value in the absence of fibres, and G_i represents the work done at the fibre–matrix interface [11]. G_i is expected to be proportional to the relative fraction of fibre–matrix interface, and should thus be proportional to V_f.

Comparing Equation 2 with Equation 1 it appears that G_m^* and G_m are about the same. Since for carbon fibres G_f is very small ($\simeq 1\,\mathrm{J\,m^{-2}}$), G_f^* can be neglected. Thus we can identify G_i with $V_f G_{fi}$, in Equation 1.

For aligned short-fibre composites, with fibre lengths L greater than the critical length L_c, G_i can be written [11]

$$G_i = \frac{V_f \sigma_{fu} L_c}{3}\left[\frac{L_c}{4L} + \varepsilon_{fu}\left(\frac{L - L_c}{L}\right)\right] \tag{3}$$

where σ_{fu} is the fibre strength (1.9 GPa) and ε_{fu} is the fibre breaking strain (0.0050). The theoretical expression given in Equation 3 assumes that some fibres break in the crack plane, and contribute to the work of fracture an amount proportional to their breaking strain. The rest of the fibres pull out instead of breaking, and frictional forces generated during pull-out contribute to the work of fracture.

Values for the fibre critical lengths are given in Table I [9]. They are all less than the length of the fibres (2 mm), as required by Equation 3. Using these values, we can estimate G_i/V_f from Equation 3 and compare the results with the values of G_{fi} obtained from the aligned fibre specimens (Table II). It is clear from the table that G_i/V_f is much greater than G_{fi}.

A possible reason for this discrepancy emerges from a look at the fracture surfaces (Figs. 3 and 5). For the theory to apply to these composites, pull-out lengths

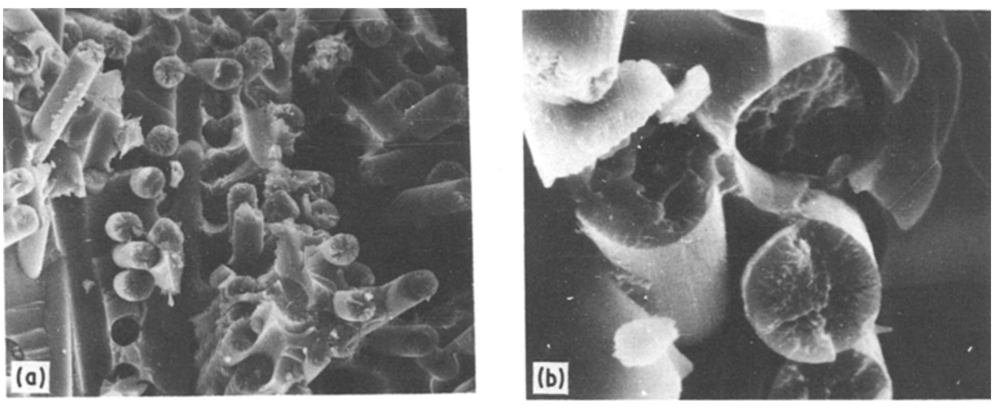

Figure 3 Fracture surfaces for aligned fibre composites. Fibres were 2 mm long, and were sized. Fibre diameter is 8.0 μm; (a) and (b) show different magnifications.

TABLE I Fibre critical lengths [9] and aspect ratios, together with interfacial shear stress (τ_i) estimated therefrom

Fibre condition	Critical length (mm)	Critical aspect ratio	τ_i (MPa)
Sized	0.72	90	21
Etched	0.89	111	17
De-sized	0.90	112	17
Silicone-coated	1.79	224	8.5

TABLE II Works of fracture and interfacial shear stress

Fibre condition	G_{fi}		G_i/V_f (Equation 3)	G_{fs} (Figs. 3 and 5)
	Aligned	Random		
Sized	17	32	42	61
Etched	17	32	64	–
De-sized	17	37	66	–
Coated	20	75*	254	57

*No linear region; estimated from results at V_f = 0.00 and 0.15.

of up to half the critical length should be observed, and average pull-out lengths should be about a quarter of the critical length. In the case of the coated fibres this comes to about 56 diameters (one quarter of the critical aspect ratio, Table II) whereas the micrograph (Fig. 5) shows much shorter lengths than this. Similarly for the sized fibres, where the average pull-out lengths should be about 28 diameters, the pull-out lengths (Fig. 3) are only a few diameters.

Clearly, the fibres were breaking quite close to the crack plane when they were expected, instead, to pull out. Since pull-out can only occur after debonding has taken place, it seems very likely that debonding was inhibited in these experiments.

Let us test this by examining the energy available for debonding. The treatment of Chua and Piggott [12] indicates that a given fibre length, L, has enough energy to debond when the fibre stress at the crack face, σ_f, is large enough that the elastic energy in that length of fibre is great enough to debond it. Thus the debonding energy, G_{fs}, can be supplied when

$$G_{fs} = \frac{d^2\sigma_f^2}{8L}\left[E_m E_f(1 + \nu_m)\ln\left(\frac{2\pi}{3^{1/2}V_f}\right)\right]^{-1/2} \quad (4)$$

where d is the fibre diameter, E_f its Young's modulus, E_m the matrix Young's modulus and ν_m the Poisson's ratio of the matrix.

The fibres must be able to supply this energy without breaking. Thus σ_f cannot be greater than σ_{fu}, the ultimate strength of the fibre. However, σ_{fu}, for these short lengths is somewhat greater than for the longer lengths used for measuring the fibre strengths.

Data on the fibre length–strength relationship is scarce. Hitchon and Phillips [13] studied Courtaulds HMS and HTS carbon fibres, and obtained results which indicated a significant decrease in strength with increasing length between 5 and 50 mm, but for lengths less than 5 mm the strength changed very little. We will adapt their results to the carbon fibres used here, by using σ_{fu} = 2.5 GPa for the short lengths of carbon fibre pulled out.

The results given in Table II were thus estimated from the average fibre pull-out lengths. They are compatible with results obtained from single-fibre pull-out studies which yield values of about 70 J m^{-2} for sized Hercules AS1 carbon fibres [14] and 4.5 J m^{-2} for silicone-coated glass fibres obtained from data given by Chua and Piggott [15] (reinterpreted using Equation 4). (The value for silicone-coated glass should be about the same as that for silicon-coated carbon.)

The relatively small amount of interface failure in the Izod test seems rather surprising, in view of the extensive interface failure that is observed when the critical fibre length is measured by extending a "composite" containing only one fibre. (In this experiment the "composite" is extended until the fibre has broken into many short pieces, and further extension causes no further fibre breakage.) In the Izod test on a normal composite, the triaxial tensile stresses at the notch promote interface failure, while in the tensile test on the single-fibre "composite", the Poisson's shrinkages do not significantly promote interface failure; the Poisson's ratio for the matrix is approximately equal to that for the fibre, at least in the case of carbon. Also, in the single-fibre "composite", consideration of the increase in compliance that results from the break-up of the fibre leads to the same expression for interface failure as that given in Equation 4.

The work of interface failure only contributes a small amount to the work of fracture. Thus for

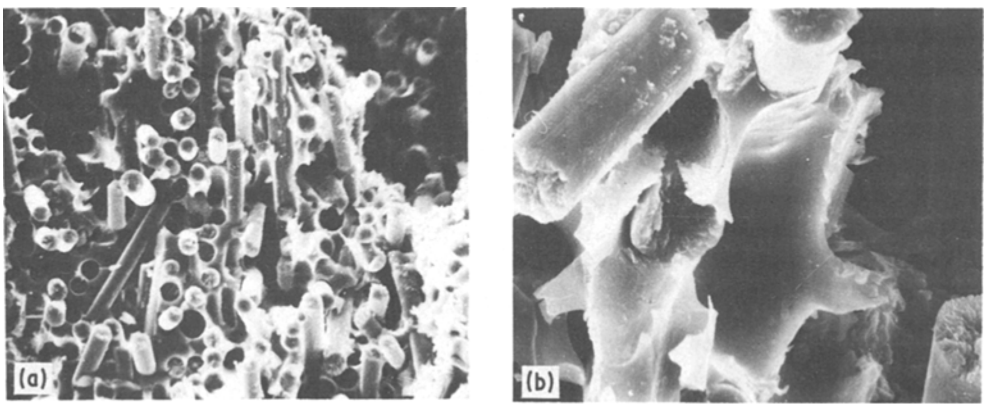

Figure 4 Fracture surfaces for random fibre composites. Fibres were 2 mm long, and were sized. Fibre diameter is 8.0 μm; (a) and (b) show different magnifications.

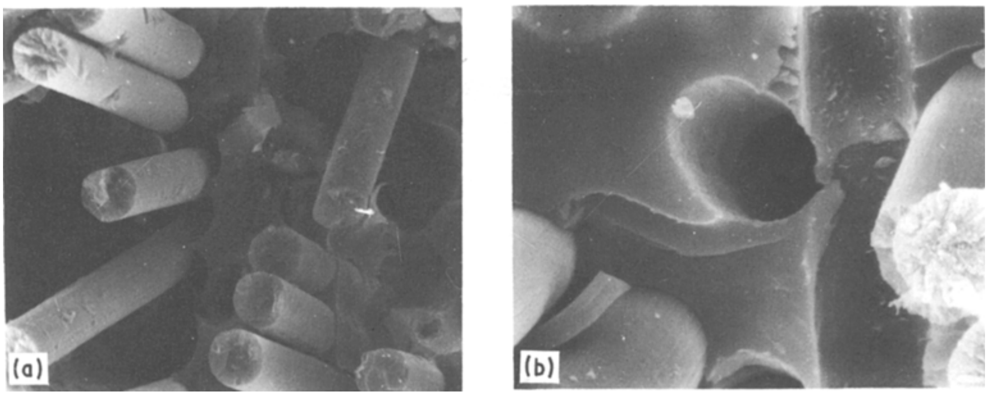

Figure 5 Fracture surfaces for aligned fibre composites. Fibres were 2 mm long, and were silicone-coated. Fibre diameter is 8.0 μm; (a) and (b) show different magnifications.

$G_{fi} = 70\,J\,m^{-2}$, and pull-out lengths of about 3 diameters the work contributed, $V_f G_{fs}$ × (pull-out length)/diameter, is less than $100\,J\,m^{-2}$.

If we assume that work done against friction during pull-out of the broken fibre ends is the main source of fracture work, as is usual [11], we can calculate the shear stress due to friction. It comes to about 70 MPa for the sized fibres (with pull-out distances of about four diameters). These values are somewhat higher than those estimated from the critical lengths (Table I) so that, if our assumption about the origin of the work of fracture is correct, Amonton's Law is not obeyed, i.e. the frictional forces are not independent of the speed of sliding. This is not very surprising, since the rate of sliding in the impact test is about 10^4 times that in the fibre critical-length measurement. In the case of the sized fibre the increase in interfacial shear stress is apparently three-fold, and the values obtained here for the shear stress are quite close to those estimated by Beaumont and Harris [16] (80 MPa) for aligned continuous carbon–epoxy. For the coated fibre the increase is only about 50%.

In the case of the random fibre composites, we expect the work of fracture to be about 6% greater than for the aligned fibre composites [11]. The results show a two- to three-fold increase. This increase is accompanied by a matching increase in fibre pull-out lengths, indicating that the interfacial shear stresses are approximately the same, but that debonding is more easily accomplished in this case.

In the case of the higher fibre volume fractions the deviations from Rule of Mixtures behaviour are somewhat similar to those observed for the composite strength [9, 10], and could be accounted for by fibre–fibre interactions at higher fibre volume fractions, as suggested by Harris and Ankara [17] for K_{Ic} for glass–polyesters.

5. Conclusions

The works of fracture of short aligned and random fibre composites are lower than expected, on the basis of measurements of fibre critical lengths. These results are interpreted in terms of the difficulty of promoting debonding in the impact test, and the resulting shorter than expected fibre pull-out lengths. During pull-out, high frictional shears appear to be present, especially in the case of the sized fibres. The values estimated are compatible with previous work, and indicate that the friction is rate-dependent.

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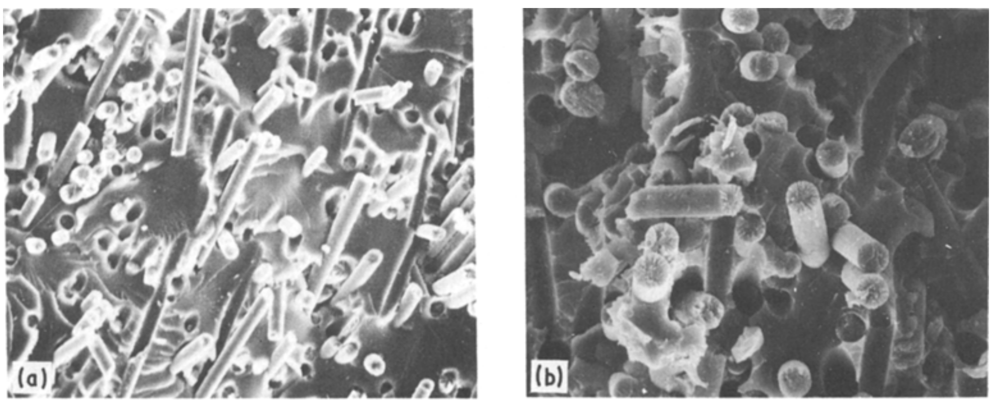

Figure 6 Fracture surfaces for random fibre composites. Fibres were 2 mm long, and were silicone-coated. Fibre diameter is 8.0 μm; (a) and (b) show different magnifications.

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