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Strength and Fracture Toughness of Carbon Fibre Polyester Composites

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Fracturing of carbon fibre/polyester composites has been studied by means of mechanical testing and scanning electron microscopy. Carbon fibres were surface-treated in several ways so as to vary the interlaminar shear strength of the composites, and the effect of this variation on the work of fracture was determined by means of Charpy V-notch impact tests and slow three-point bend tests on notched specimens of triangular cross-section. The effect of moisture on the fracture toughness was also studied by measuring toughness and interlaminar shear strength after exposure to steam. Improvement of the fibre/resin bond results, as expected, in an increase in the brittleness of composites and it appears that a purely mechanical bond, such as might be obtained by acid-etching the fibre surface, is less proof against deterioration in humid atmospheres than a chemical bond, such as can be obtained by the use of coupling agents. Estimates of the magnitude of various contributions to the fracture toughness show that in carbon-fibre-reinforced resins the effect of increasing the stiffness or load-bearing ability of the matrix and the work done against friction in pulling broken fibres out of the matrix contribute approximately one fifth and four fifths, respectively, of the total work of fracture.

1. Introduction

Strong carbon fibres aligned in polymer matrices give composites with high specific strength and stiffness, a primary design criterion; and with the aid of suitable fibre surface-treatments the otherwise low interlaminar shear strengths of such composites can be varied to suit most other design requirements. Two of the most serious drawbacks of glass-fibre-reinforced plastics can therefore be overcome. Underlying the subsequent problems of how these composites respond to complex modes of stressing, to load-cycling, and to chemically active environments is the important question, at present being widely studied, of how the materials fail on a local scale. In this work we have fractured carbon-fibre composites in a variety of mechanical tests and studied the effects of fibre surface treatments upon the properties measured. We have also examined fracture surfaces of broken specimens with the scanning electron microscope in an attempt to detect local variations in fracture mechanism resulting from surface treatment and different modes of stressing. Finally, we have attempted to analyse our results in the light of various theories of fracture of composites in order to discover the main contributions to the fracture energy.

2. Materials

Two types of specimen have been used. Flat bars of varying thickness were made by impregnating a weighed quantity of fibre with liquid resin under pressure in a mould of fixed volume. Excess resin was slowly expelled and finished bars were of constant composition at a volume fraction of 0.40. For compression tests and Charpy impact tests rod samples were prepared by slowly pulling resin-soaked tows of fibre into a glass tube with a flared end. Excess resin and entrapped air were expelled in the process, giving composites, again of $V_f = 0.40$, with low porosity. The resin system was Bakelite SR 17449 with MEK peroxide catalyst and cobalt naphthanate accelerator in the ratio 100:2:2, and the fibre was Morganite type I (high modulus) fibre,

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7.93 ($\pm$ 0.61) $\times$ 10^{-6} m in diameter with a tensile strength of 1.58 ($\pm$ 0.44) GN m^{-2}, and Young's modulus of 360 ($\pm$ 31) GN m^{-2} (figures in brackets are standard deviations). All composites were cured at room temperature and post-cured at 100°C for 16 h.

3. Fibre Surface Treatment

The low interlaminar shear strength of composites containing high-modulus carbon fibres has been demonstrated by Simon *et al* [1], and there have been various reported attempts to improve upon these low values. There appear to be three basic methods. The surface may be treated so as to produce a chemical bond between resin and fibre, such as occurs when silane coupling agents are used in glass-filled resins. Treatments of this kind applied to carbon fibres have been described by Harris *et al* [2]. Alternatively, the fibre surface may be roughened so as to increase mechanical keying between resin and fibre. By attacking the fibre with oxidising agents the surface can be etched, and provided the etching is uniform the shear strength should be improved without any concomitant reduction in tensile strength. Experiments on surface oxidation have been described by Herrick *et al* [3, 4] and Novak [5]. The inverse process has been carried out by Simon and Prosen [6], who grew silicon carbide whiskers upon the fibres and raised both the shear strength of the composite and the price of the fibre by several orders of magnitude. However, this treatment also drastically reduces the tensile strength of the fibre and must at present be considered unsatisfactory. High shear strengths are offered with British commercial fibres, through as yet unidentified surface treatments. For the experiments described in this paper the following treatments were used to give modest increases in the interlaminar shear strength:

(*a*) Fibre was boiled for 2 h in 70% nitric acid, followed by washing in water and drying. No weight change occurred during this treatment.

(*b*) Fibre was dipped into a 12% solution of 702 silicone fluid in acetone, followed by evaporation of the solvent. The purpose of this treatment was to surround the fibre with an inert film which would reduce the interlaminar shear strength.

(*c*) Fibre was exposed to bromine vapour (in contact with liquid) for seven days in a closed tube, the air pressure having previously been reduced slightly to assist vaporisation of the bromine. A slight increase in weight, of the order of only 0.1% was observed.

(*d*) Some of the fibre that had been boiled in nitric acid was coated with an epoxy silane (Union Carbide A186) by dipping into a 30 vol.% solution of the silane in MEK. This treatment has already been fully described [2].

4. Mechanical Properties

4.1. Test Methods

Conventional tensile, flexural, and short-beam interlaminar shear properties were measured on all flat bar samples. For tensile tests aluminium tabs were glued to the ends of specimens whose gauge sections had been reduced in cross-section until a sharp fracture normal to the tensile axis could be obtained. The span-to-thickness ratio for three-point bend flexural tests was 25:1, while that for interlaminar shear tests was 5:1. Modes of failure in these two tests were consistently tensile and shear, respectively. Satisfactory compression testing is not easily carried out on composites. In free-standing column tests on many types of composite, compression strengths as high as the tensile strength can be measured, but when the reinforcing fibre is brittle and the strength of the interfacial bond is low, the compression strength generally falls below the tensile. We have nevertheless carried out some free-ended column tests, between flat-ground anvils lubricated with PTFE tape, to study the effect of interfacial bond strength on the mode of fibre and composite failure rather than to measure any true, design compression strength.

4.2. Results

Table I contains the results of tensile and long-beam flexure tests which, ideally, should measure the same property.

Given satisfactory specimen shape and gripping arrangements, the tensile strength of composites should be independent of surface treatment provided the treatment has not modified the fibre properties. In a 0.40 V_f composite the average fibre-breaking stress is being developed if the composite has a mean tensile strength of 0.623 GN m^{-2}. The strengths of three out of the five types of material represented in the table are therefore quite satisfactory, but bromination has apparently damaged the fibre, for both tensile and flexural strengths of these composites are reduced. It has been suggested by Martin and Brocklehurst [7] that the entry of bromine into graphite can lead to splitting, because the bromine enters small fissures parallel with the basal planes. Rüland

TABLE I Tensile and flexural strengths of some CFRP

Material	Tensile test			Flexural test, span/thickness = 25:1		
	Tensile fracture stress (GN m^{-2})	No. of tests	Range (GN m^{-2})	Tensile stress in outer fibres at fracture (GN m^{-2})	No. of tests	Range GN m^{-2}
Polyester + untreated fibre	0.725	2	0.71–0.756	0.495	1	—
Resin + fibre-boiled in HNO_3	0.710	4	0.64–0.852	0.535	1	—
Resin + brominated fibre	0.582	4	0.48–0.648	0.450	3	0.41–0.494
Resin + silane-coated fibre	0.625*	—	—	0.520*	—	—

*Data from Harris *et al* [2], for comparison.

and his colleagues [8] have demonstrated the existence of fine, tubular pores between the "wrinkled ribbon" constituents of carbon fibres, and the opening up of these pores by bromine could lower both the tensile and bending strength of the fibre and, consequently, of the composite.

Bend tests on brittle materials are usually found to be more reproducible than tensile tests because the effects of flaws and geometrical stress concentrations are reduced. For this reason flexural test results are usually higher than the corresponding tensile strengths of identical samples. In these composites, however, the reverse is true. If the compressive strength of CFRP is lower than the tensile strength, failure could be initiated by crushing of the fibres on the compressive surface before those on the tensile face can fail in tension. There is evidence that this is the correct explanation. In bend tests discontinued before final separation of the pieces it was usually found that the compression face was fractured, but that the pieces were still held together by unbroken fibres in the tensile surface. Scanning electron microscopy shows that at the compression face the fibres are crushed whereas on the tensile side the fracture has the normal brushy appearance (fig. 1) It has been suggested that this crushing failure could be caused by an excessively sharp-nosed punch in the bending jig, but we have also observed failure on the compressive face in samples being fatigued in flexure where there is no point of contact with a punch. Furthermore, like Novak [5] we found that the compressive strengths of these composites in tests on free-standing cylinders is very low. The invariable mode of failure was for a longitudinal crack to appear at one of the free ends of the

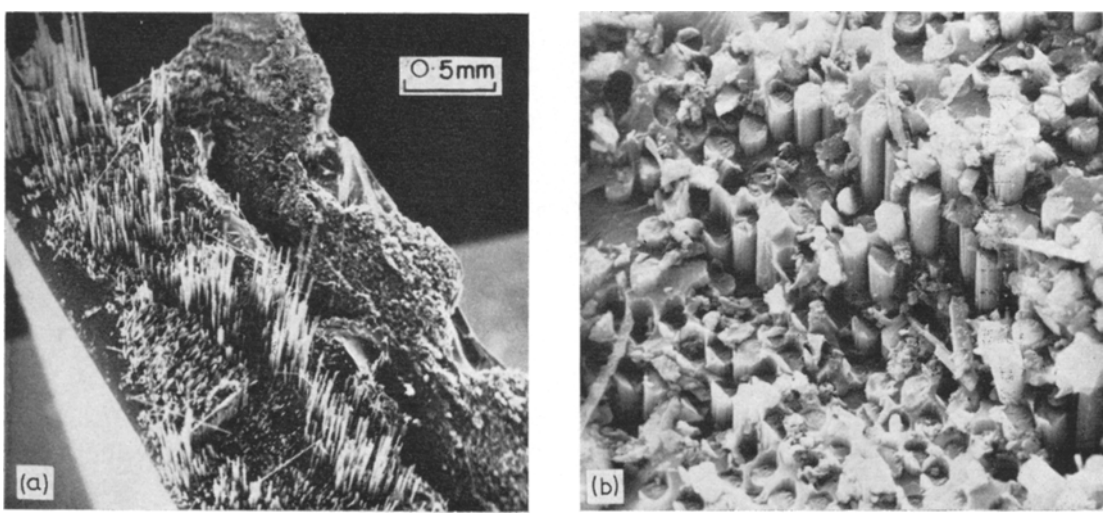

Figure 1 SEM photograph of the fracture surface of a flexure test specimen of a carbon fibre composite. (*a*) complete view and (*b*) higher magnification view of compression side showing short, crushed fibre ends and much debris.

TABLE II Compressive strength of some composites.

Material and fibre treatment	Mean failure stress (GN m^{-2})	Number of samples	Range (GN m^{-2})
Polyester resin	0.116	8	0.103–0.121
Resin + untreated fibre	0.095	5	0.084–0.122
Fibre boiled in HNO_3	0.088	3	0.074–0.098
Fibre treated with silicone fluid	0.094	8	0.070–0.110
Brominated fibre*	0.125	6	0.096–0.167

*For these samples $V_f \sim 0.30$ because of difficulties in packing brominated fibre into the tubes. The failure stress is the measured value, uncorrected for this difference in V_f.

cylinder and the two halves so formed were then gradually separated, the fibres being slowly fragmented through local bending. The results of some compression tests are given in table II.

In most cases the addition of fibre merely weakens the resin. If there is no chemical bond the fibres may become unbonded from the resin when the composite is loaded in compression and the result is a resin sample full of holes. However, for a resin containing 0.40 V_f of holes the sample failure stress, based on that of the pure resin, should be only 0.069 GN m^{-2}, so we conclude that immediate debonding does not occur. The supposition that it occurs at all implies that the resin has a Poisson's ratio greater than the fibre. This has not yet been confirmed, but there is evidence that the Poisson's ratios for fibre and resin are not very different since, in fact, the elastic moduli of composites fall very close to rule-of-mixtures predictions.

A further hint of the potential danger of using CFRP under compressive loads is given by the behaviour of single fibres loaded in compression in a resin matrix. The fibres do not buckle, as various other fibres have been shown to do in silicone rubber matrices [9]. As fig. 2 shows, the fibres break regularly into short sections, the individual fractures being part shear and part transverse.

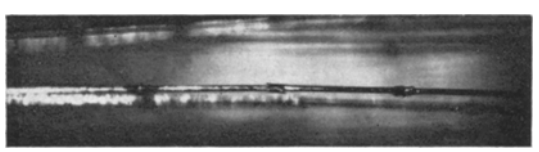

Figure 2 Fractures in a single fibre, loaded in compression in resin.

TABLE III Interlaminar shear properties of CFRP.

Material	Interlaminar shear strength (MN m^{-2})	Number of tests	Range (MN m^{-2})
Resin + untreated fibre	20.4	4	18.35–22.0
Fibre boiled in HNO_3	24.2	3	22.7–25.3
Fibre treated with A 186 silane	27.2*	—	—
Fibre treated with silicone oil	11.5	2	10.7–12.25
Brominated fibre	24.3	6	23.3–25.5

*Value from Harris *et al* [2], for comparison.

Table III shows that with the aid of various surface-treatments the interlaminar shear strength can be quite widely varied. The highest shear strength, some 33% greater than that of untreated fibre composites, is obtained from the silane treatment, as discussed previously [2]. Bromination and the acid etch both raise the shear strength by about 20%. The presence of silicone oil reduces fibre/resin adhesion, as expected. For comparison with the other data in table III we quote a value of 46 MN m^{-2} from Morganite, given by Peters [10] for commercially-treated type I fibres in an unspecified matrix. We have ourselves measured values as high as 55 MN m^{-2} on polyester/type I carbon composites (V_f = 0.40), but this is almost certainly too low because even with the smallest span-to-depth ratios available in the short-beam shear test, failures were usually part tensile, part shear.

5. Work of Fracture

5.1. Methods

Three methods have been used to measure the work of fracture, γ_F, for most of the composites previously described, in an attempt to discover in what way consistent results may be obtained for composite materials and how far the ideas of fracture mechanics may be applied to the case of a non-linear, inhomogeneous, anisotropic solid. The simplest test used was the impact of cylindrical V-notched specimens in a Hounsfield miniature Charpy machine of 2.75 J capacity and striker velocity of 2.54 m sec^{-1}. Specimens were of the dimensions given in fig. 3. Measurements of energy absorbed during fracture were made on samples with machined notches and on others in which the machined notches had been sharpened with a scalpel. The effect of notch depth was also studied. In view of the fact that the speed of

crack propagation is relatively low and the two halves of the specimen are flung away from the machine after impact at velocities of only a few metres per second, the kinetic energy lost in this way is quite small. Typically, the specimen weighs 2×10^{-3} Kg and is flung away at some 2 m sec^{-1}. The kinetic energy is therefore $\sim \frac{1}{2}.(2 \times 10^{-3}).(2)^2$ Joules, or roughly 0.004 Joules. Over twice the sample cross-sectional area this amounts to about 80 J m^{-2}, which is negligible in comparison with the values of 30 KJm^{-2} measured for γ_F. Other impact tests were carried out on U-notched flat bars (fig. 3b) in an instrumented drop-weight machine of 27.5 J capacity and striker velocity 4.6 m sec^{-1}. Load/time traces from the oscilloscope were used to determine the work of fracture and these traces were used in a comparative, rather than an absolute, sense to study the effect of exposure to moisture. Slow bend tests were carried out in the manner of Tattersall and Tappin [11] on square bars cut so as to leave a triangular cross-section (fig. 3c). A crack starts at the point of high stress concentration at the apex of the triangle and passes in a controlled manner across the sample. Integration of the load/deflexion curve again gives γ_F.

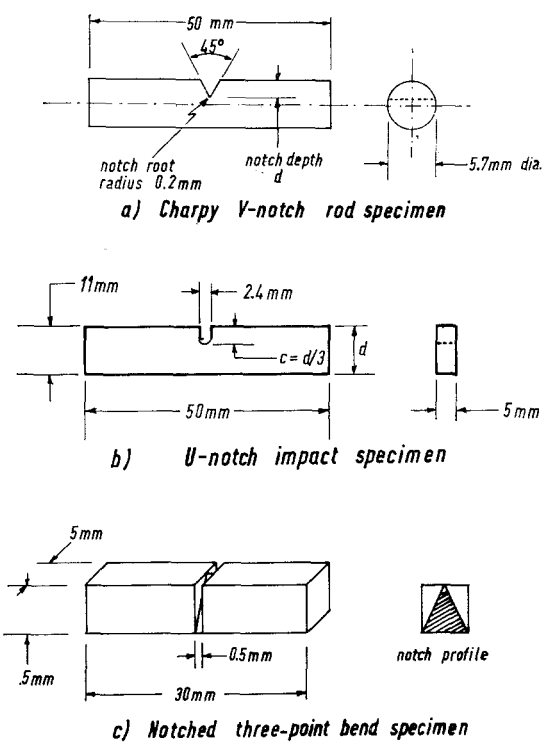

Figure 3 Dimensions of fracture test specimens.

5.2. Results

There are difficulties in the interpretation of the data about to be discussed. In an experiment to measure the change in compliance with crack length, the work of fracture is given by the critical strain energy release rate, G_{IC}:

$$2\gamma_F = G_{IC} = \tfrac{1}{2}P^2 \frac{d(1/k)}{dA} \qquad (1)$$

where P is the force on a plate specimen containing a crack of surface area A for which the spring constant is k. This derivation does not involve the surface area of the crack, but in the Charpy test, or the slow bend test used here, the work of fracture is given as the energy absorbed from the pendulum or the area under the load/deflexion curve divided by the total surface area of the crack. If the fracture is clean and flat, the surface area is twice the area of the fractured cross-section. In composites, however, this is often difficult to arrange. In the Charpy test the mode of failure was almost always a mixture of tensile and shear failure as shown schematically in fig. 4.

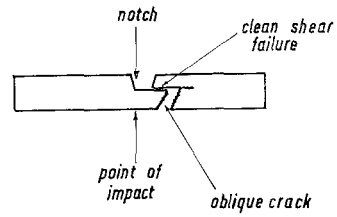

Figure 4 Schematic drawing of a fractured Charpy specimen.

An interlaminar crack propagates from the notch and is joined at some distance from the notch by an oblique, transverse crack emanating from a point on the *back* face, which was not usually the point of impact. In specimens with deep notches the sheared face was clean, flat and of about the same area as the rod cross-section, whereas in specimens with very shallow notches shearing was much more extensive and the fracture more ragged. Fig. 5 shows the actual fractures obtained in drop-weight tests, which show similar behaviour. In untreated fibre-composites the angle of the transverse crack is about 45° to the line of striking, but as the interlaminar shear strength is raised by surface treatment, the angle becomes more acute until the crack propagates normally from the notch root. On a local scale the oblique fracture can be resolved into a series of alternate

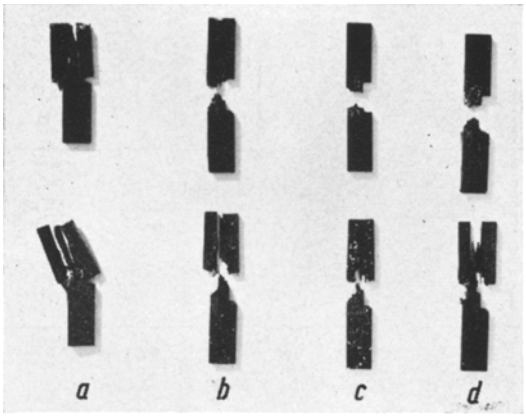

Figure 5 Fractures of U-notched specimens broken in the drop-weight test.

components of tensile and shear failure (figs. 6a and b). In the tensile steps in fig. 6 the resin can be seen to be cracked obliquely although the fibres have failed normal to the tensile axis.

The question that must now be asked is how the work of fracture can be computed, given this complexity of crack surface topography. In the slow-bend test matters are improved because the crack is forced to propagate in a single plane whose area can be measured. But even here, since failure is still accompanied by the pulling out of many fibres, the cross-section area may be far from the true area of the fracture surface. We shall see, however, that in the two types of test, and even when the amount of shearing changes considerably from one Charpy test to another, the measured values of γ_F are not very different. It may be permissible to assume, therefore, that the work lost in shearing the composite is very small compared with the work of fracturing the composite in tension and pulling fibres out of the matrix. We have in fact observed in recent experiments on carbon fibre/epoxy resin composites that γ_F for crack propagation normal to the fibres in a wide plate where no shearing is allowed to occur is also roughly 30 KJm^{-2} and is two orders of magnitude greater than γ_F measured in a slow bend test for propagation parallel with the fibres. All values of γ_F given here have therefore been determined using twice the area of cross-section of the sample in the plane of the notch.

5.2.1. Charpy Impact Tests

In fig. 7 values of γ_F for untreated fibre composites are given as functions of notch depth for samples with machined notches and with knife-sharpened notches. The results echo those of Harris and Ferran [21] for polyester resin. They show that scatter can be reduced by sharpening the notch and that the work of fracture is a minimum for notch depths about a third of the rod diameter (at which point the degree of shearing in the sample is also small). The variation is small, however, and too ill-defined at this stage to justify treating it as a real effect: in what follows, therefore, we shall use averages taken over a range of notch depths. Table IV lists mean values of γ_F obtained from Charpy tests for several types of treated fibre. Apart from the

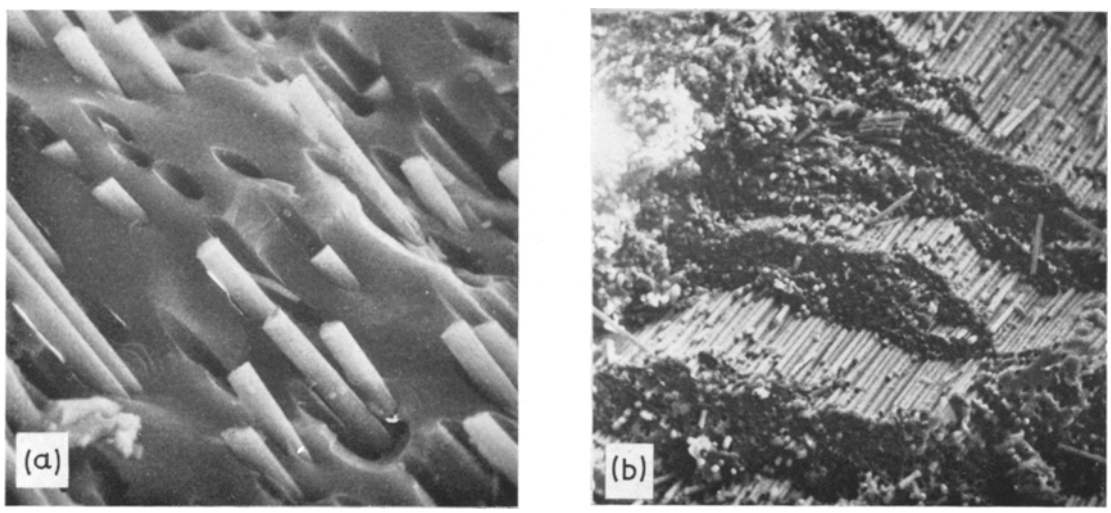

Figure 6 Stereoscan photographs at low and high magnification of the oblique fracture surface usually obtained in impact tests on specimens with relatively low interlaminar shear strength.

TABLE IV Work of fracture of CFRP.

Fibre treatment	Charpy test: Mean γ_F, KJ.m^{-2}				Slow bend tests; γ_F, KJ.m^{-2}
	machined notches	No. of tests	sharpened notches	No. of tests	
Untreated	30.4	9	33.3	8	32.3; 35.8
Boiled in HNO_3	27.8	3	28.8	3	30
Silane treated	23.7	2	29.3	2	20.1; 21.6
Brominated	30.3	2	23.6	3	35.9; 31.5
Silicone oil	28.4	2	34.8	2	—
Morganite treated	—	—	8.8	4	—

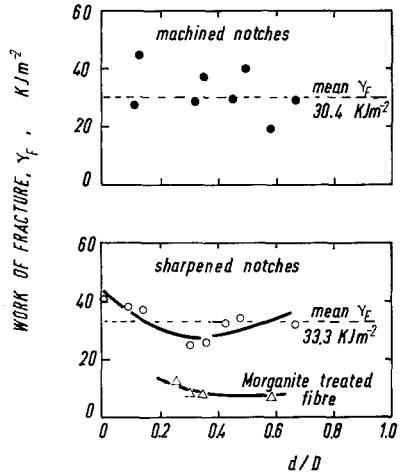

Figure 7 Work of fracture, γ_F, for composites containing untreated carbon fibre, measured in Charpy pendulum impact tests.

effect of surface treatments shown in the table the interesting fact emerges that in all cases but one, the effect of sharpening the notches was to increase the work of fracture rather than to decrease it as was found by Harris and Ferran in unreinforced polyester resin.

5.2.2. Slow Bend Tests

The results from these tests, shown in table IV, are close to the Charpy measurements of energy absorbed from the pendulum, despite the substantial differences in appearance of the fracture surfaces. But in the case of the triangular-notched sample there is no ambiguity about the crack surface area. A composite sample in the slow bend test is, as we have pointed out, forced to crack in the plane defined by the saw cuts, but in the Charpy test it will frequently fail by a complex mixture of shear and tensile failure. It is upon this fact, and the similarity of γ_F values from the two tests, therefore, that we justify our reasoning that the shearing component of failure alters only slightly the total work of fracture.

Load/deflexion traces for the cracking of the four materials are shown in fig. 8. One curve stands out from the rest: the silane-treated fibre

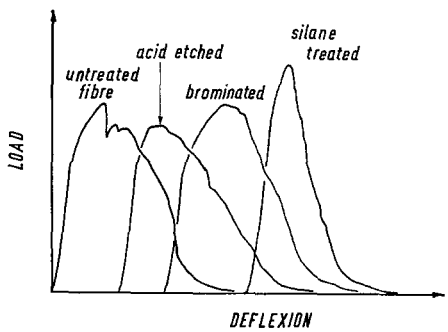

Figure 8 Load/deflexion traces obtained during slow-bend tests on triangular notch specimens.

sample requires less work for fracture than any of the others, but requires a higher stress to start the crack.

5.2.3. Drop-weight Tests

Fractures in these rectangular bar samples were similar in most respects to those of the Charpy tests. As fig. 5 showed, there was a reduction in the amount of shearing as the fibre/resin bond was improved to the point where, in the silane-treated material, the fracture propagated normally across the bar, with an irregular surface but without shear. Typical oscilloscope traces are shown in fig. 9, and again it can be seen that the silane-treated material behaves quite differently from the others, the trace being smooth, with a single hump, whereas the other samples give jerky traces. The peak load is also lower than that of the other samples. This instrument has so far been used for comparative work only, but the

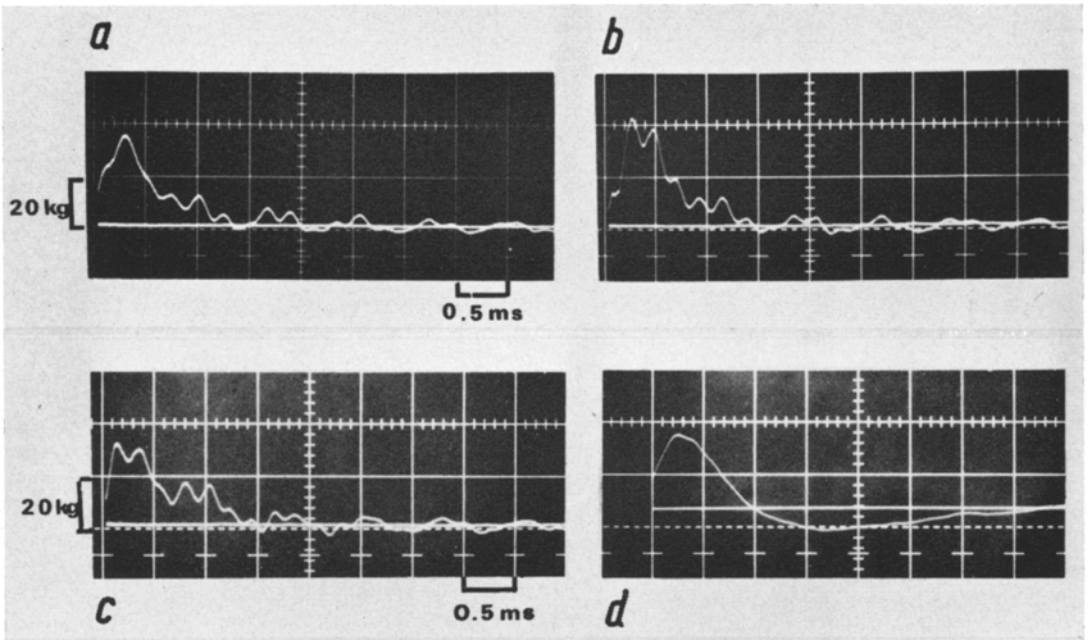

Figure 9 Oscilloscope traces showing load versus time traces obtained from impact tests on various carbon fibre composites using the instrumented drop-weight machine.

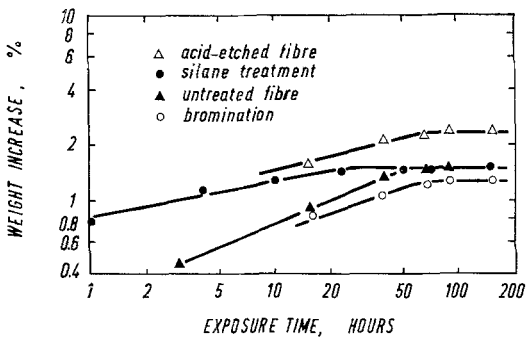

Figure 10 Change in weight of carbon fibre composites during exposure to steam at 100°C.

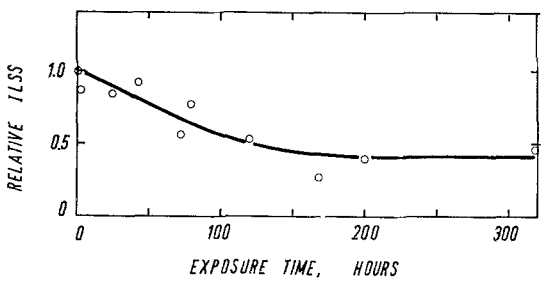

Figure 11 Effect of exposure to steam at 100°C on the interlaminar shear strength of untreated fibre composites.

areas under the oscilloscope traces for the untreated, acid-etched, silane-treated and brominated fibre composites are very closely in the same ratios to one another as the mean values of γ_F, measured by the other two methods, given in table IV.

6. Effect of Moisture

A selection of samples was exposed to steam at 100°C for seven days and the change in work of fracture was determined by the drop-weight method. The net change in weight during exposure, which is the sum of an absorption of moisture by the composite plus a loss of volatile constituents from the resin, is shown in fig. 10. The rate of weight increase and the total overall increase are greater for the acid-etched fibre composite than for any of the others which all behave roughly alike except for the initial high rate of weight-increase for the silane-treated material. This increased susceptibility to moisture ingress may be a result of increasing the surface area by etching. The effect of moisture on the interlaminar shear stress of the untreated fibre composite is shown in fig. 11. After about a week the shear strength has reached a stable value roughly half that before exposure. Table V shows the effect of steam on the work of fracture for four of the composites. All surface-treatments bring about some improvement in resistance to

TABLE V Effect of exposure to steam on work of fracture.

Surface treatment of fibre in composite	Percentage of γ_F retained after exposure to steam for 1 week
Untreated fibre	49%
Brominated fibre	56%
HNO_3 etched fibre	83%
Silane treated fibre	100%

moisture absorption, but the silane treatment appears to prevent any deterioration whatsoever. The change in weight of a control sample of polyester resin exposed to steam for a week was almost nothing. We can probably assume, therefore, that the observed change in weight in the composites is largely due to the drawing-in of moisture along the interface, which effectively separates the surfaces of the resin and fibre and lowers the interlaminar shear strength. If there is a covalent bond between resin and fibre, however, as may be the case in silane-treated composites, the water film is unable to destroy this bond as it does a purely mechanical one and the work of fracture is not reduced. Except in this instance, therefore, there must already be extensive debonding before the impact test is conducted and the resulting fractures would be expected to show large amounts of shear failure. This can be seen in fig. 5. Stereoscan pictures such as those in fig. 12 always show that the mean pull-out length of the fibres is much greater after exposure to steam than before.

Some corroborative experiments on the effect of exposure to steam have been carried out by Mr K. Phillips, formerly of the University of Sussex. Phillips prepared samples of treated and untreated fibre composites 62 × 9.6 × 1.45 mm and took them through slow reversed cycles of torsional loading in apparatus of the kind used by McCrum and Morris [12]. He measured the torsion modulus and the hysteresis loss (from the area of the closed loop) for very small deflexions (maximum shear strains of about $\pm$ 0.01). The results for exposed and unexposed samples are given in table VI. The torsion modulus is much less drastically reduced after exposure if the fibres have been treated, but the silane treatment and acid-etching produce roughly the same improvement. The hysteresis loss in these materials may be due to reversible sliding of the resin past the fibres. A chemical bond, such as we believe to be present in the silane-treated material, does not seem to inhibit sliding in dry conditions better than a purely mechanical bond, such as that produced by acid etching, but by reducing moisture build-up at the resin/fibre interface it appears to be a superior treatment for service in humid environments.

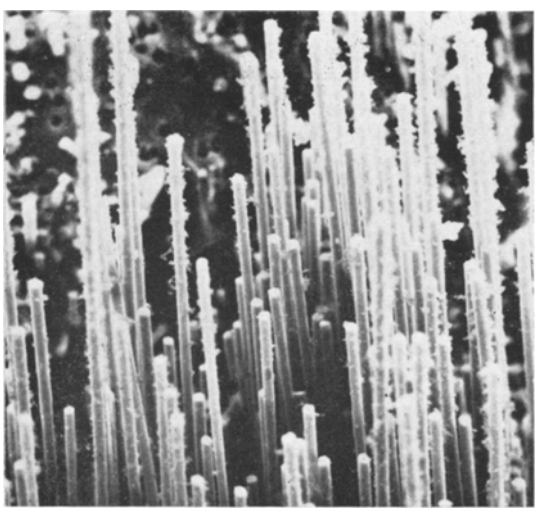

Figure 12 Stereoscan picture of the fracture of a carbon fibre composite after exposure to steam for one week.

7. Discussion

Work of fracture and interlaminar shear strength are both affected by treatments which alter the fibre surface characteristics, either mechanically or chemically, in such a way as to change the strength of the interfacial bond or otherwise augment mechanical friction between fibre and resin. We have measured neither the bond strength nor the friction directly and it is difficult to be precise about the lengths of pulled-out fibres seen in fractographs. But the indirect relationship between toughness and interlaminar shear strength can be examined and is indeed of considerable importance to the designer. From fig. 13 it can be seen that high values of these two vital engineering parameters are mutually exclusive and the designer must be prepared to compromise to some extent. As Cottrell [13] and Mullin *et al.* [14] point out, it is desirable to have an interfacial bond strength sufficiently high to allow the average filament strength to be just reached in the fibres. This permits the matrix to unbond at newly-created fibre ends instead of causing matrix tensile fractures, and does not lead to immediate fracture of neighbouring fibres. Cook and Gordon [15] show that if the interface adhesive strength is greater than about a fifth of the matrix cohesive stress, cracks will

TABLE VI Torsional modulus and hysteresis loss results

Material	Prior to exposure to steam		Exposed to steam for 1 week	
	Torsion modulus (GN m^{-2})	Hysteresis loss*	Torsion modulus (GN m^{-2})	Hysteresis loss*
Untreated fibre	2.40	1.0	1.62	2.41
Fibre etched in HNO_3	2.32	1.01	2.05	1.67
Brominated fibre	2.12	1.37	—	—
Silane treated fibre	2.30	0.97	1.96	1.38

*Recorded as a fraction of the value for untreated fibre composites prior to exposure to steam.

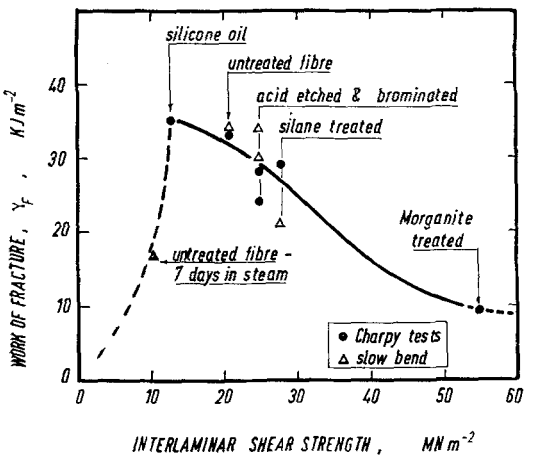

Figure 13 Effect of surface treatments on the interlaminar shear strength and work of fracture of carbon fibre composites.

propagate directly through resin and fibre, no debonding will occur, and the composite will behave as a homogeneous brittle solid with low fracture toughness. On the other hand, if the interface is too weak the material will have negligible strength, like graphite or talc. The curve in fig. 13 should therefore fall rapidly at low interlaminar shear strengths towards a low value of γ_F representative of the "toughness" of a bunch of brittle, unbonded fibres. As fig. 11 and table V show, exposure to steam of untreated fibres causes both fracture toughness and interlaminar shear strength to be roughly halved and the pull-out lengths are much greater.

Various contributions to the work of fracture of composites have been discussed, and it is interesting to compare some of them with the results just described.

Outwater and Murphy [16] have pointed out that the toughness of glass-fibre-reinforced plastics (GRP) can be as high as 100 KJm^{-2}, several orders of magnitude greater than that of glass (5 J m^{-2}) and polyester resin (200 J m^{-2}). The same applies to carbon-fibre-reinforced plastics (CFRP) since the work of fracture of carbon is also about 10 J m^{-2}. This can be obtained from the theoretical strength and surface energy calculations given, for example, by Kelly [17], where the surface energy

$$\gamma_S \approx Ea_0/10 \approx 6 \text{ J m}^{-2}$$

a_0 being the C–C length.

Outwater and Murphy [16] argue that the high toughness of GRP stems entirely from the work of debonding the fibres from the resin in the course of propagation of a crack. Using a fracture-mechanics approach they obtain, for the strain energy release rate G_I,

$$G_I = \frac{V_f \sigma_f^2}{2E_f} \cdot y \qquad (2)$$

where y is the length of filament that becomes debonded during the fracture process. If we assume that y will be about twice the mean pull-out length, which we will refer to as $\bar{x}$, and let $G_I = 2\gamma_F$, then we obtain, for our CFRP,

$$\gamma_F \approx \frac{0.4 \times (1.6 \times 10^9)^2}{2 \times 360 \times 10^9} \cdot \bar{x} \text{ J m}^{-2}$$

$$\approx 1.5 \times 10^6 \cdot \bar{x} \text{ J m}^{-2}$$

From stereoscan pictures, such as the low magnification ones in fig. 14, it can be seen that $\bar{x}$ is between 10 and 50 fibre diameters, which puts γ_F between 120 and 600 J m^{-2}, some two orders of magnitude below the measured values of γ_F. Indeed, in order to obtain a measure of agreement with Outwater's model, fibre pull-out lengths of the order of 2 cm would have been required.

Cottrell [13], Kelly [18], and Cooper and Kelly [19] have considered the amount of work required to pull the ends of fibres broken by the passage of a crack out of the matrix as the specimen is fractured. An advancing crack does

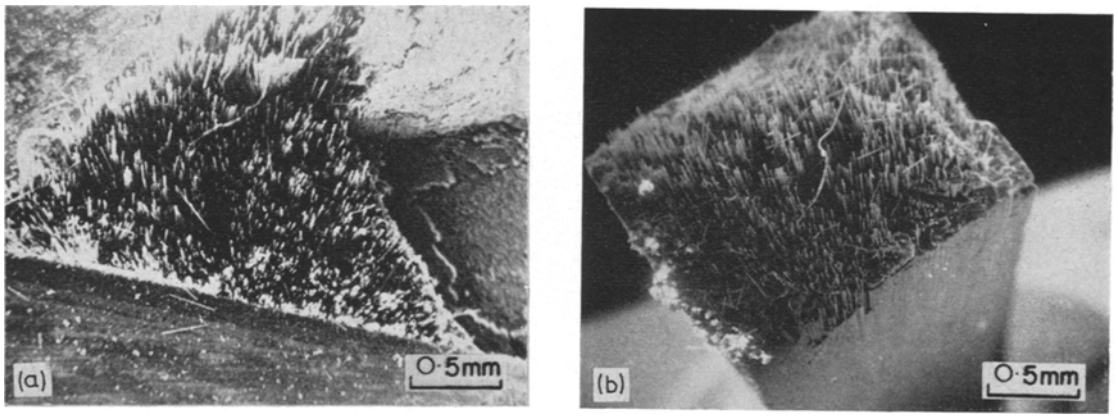

Figure 14 Low magnification Stereoscan photographs of fractures in (*a*) triangular notched bend specimen and (*b*) tensile test specimen of carbon fibre composites.

not necessarily fracture a fibre at a point in the plane of the crack because the lateral stress concentration, which is tensile and normal to the interface, causes some debonding ahead of the crack tip and exposes a considerable length of fibre to an unconstrained "tensile test" [15]. The fibres may remain unbroken while the crack advances past them (particularly if they have a high breaking strain like glass) but they will ultimately break at some flaw in the fibre within the debonded length. As the crack passes on, leaving the composite behind the tip largely unstressed, the resin and fibres are allowed back into contact, and the broken fibres must then be pulled out of the resin in order to separate the two halves of the specimen. Cottrell [13] and Kelly [18] determine the work needed to pull the fibres out while Cooper and Kelly [19] and Cooper [20] extend the simple model so as to consider the effect of the spacing and distribution of flaws in the fibres. We have no quantitative data of this kind for carbon fibres and we shall therefore consider only the result of the simple calculation first given by Cottrell.

By equating the fibre breaking load with the interfacial friction force, he obtains for the work done per unit area of cross-section

$$W/A = \frac{V_f \sigma_f}{12} \ell_c \qquad (3)$$

Assuming that $\ell_c/2$ is roughly equal to the maximum obtainable pull-out length, the observed pull-out length will vary between 0 and $\ell_c/2$. The mean observed pull-out length, $\bar{x}$, which was about 30 fibre diameters in untreated fibre composites, is equal to $\ell_c/4$. For the work of fracture, therefore, we have:

$$\gamma_F = W/2A$$
$$\approx \frac{0.4 \times 1.6 \times 10^9 \times 120 \times 8 \times 10^{-6}}{24} \quad \mathrm{J\,m^{-2}}$$
$$\approx 26 \ \mathrm{KJ\,m^{-2}}$$

This crude estimate gives the maximum contribution to the fracture work from fibre pull-out. In composites containing brittle fibres, such as carbon, fibres will often fracture at flaws which, in many cases, will mean that the average pull-out length will be less than $\ell_c/4$ and the contribution to the work of fracture from friction will be less than that given by equation 3. However, since we have based our arithmetic on a visual estimate of pull-out length, the process of arriving at this estimate will be the principal source of our error. The result does suggest, however, that the frictional work plays a dominant role in determining the fracture energy.

When the fibre/resin bond is substantially improved by fibre surface treatments it becomes more difficult to pull fibres out of the resin and it would appear, at first sight, that the fracture toughness must increase because the frictional work increases. However, the basic relationship between the critical length/diameter ratio, ℓ_c/d, the fibre fracture stress, σ_f, and the interface friction stress, τ_i;

$$\ell_c/d = \sigma_f/2\tau_i$$

means that the pull-out length must decrease as the friction stress increases. If equation 3 is then rewritten as:

$$\gamma_F = \frac{V_f \tau_i \ell_c^2}{12d} \qquad (4)$$

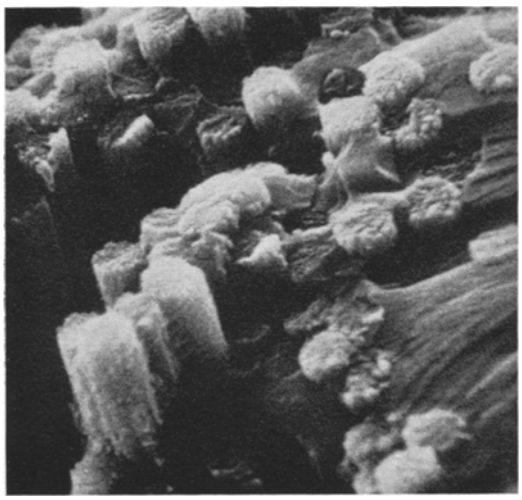

Figure 15 Fracture surface of a composite containing carbon fibres heavily oxidised by heating in air.

we see that the dependence on ℓ_c is the stronger, and the work of fracture must fall with increasing fibre/resin bond strength. If the bond strength is sufficiently increased so that no debonding can occur ahead of the crack and there is no fibre pull-out, the toughness of the composite must be due to sources other than frictional work. We have observed that composites prepared from commercially-treated fibres or fibres heavily oxidised by heating in air [2] invariably break with brittle, tensile fractures, even in short-beam shear tests with very small span/depth ratios, and the fibre pull-out lengths are of the order of only one or two fibre diameters (fig. 15). Equation 3 indicates that for this condition the frictional contribution is only of the order of 2 KJ m^{-2} so that of the measured 9 KJ m^{-2} for the Morganite-treated fibre composites, 7 KJ m^{-2} is derived from some other source. This is in good agreement with the previous estimate, since we then have that of the total 33 KJ m^{-2} for untreated fibre composites, 26 KJ m^{-2} are contributed by frictional work and the remaining 7 KJ m^{-2} is for the toughness of a composite which breaks without pull-outs. The form of a curve of toughness as a function of the product $(\tau_i \ell_c^2)$, as given by equation 4, is shown schematically in fig. 16. This can easily be made to approximate the shape of the γ_F versus interlaminar shear strength curve of fig. 13. It also shows why the effect of exposure to steam is to reduce both γ_F and the ILSS.

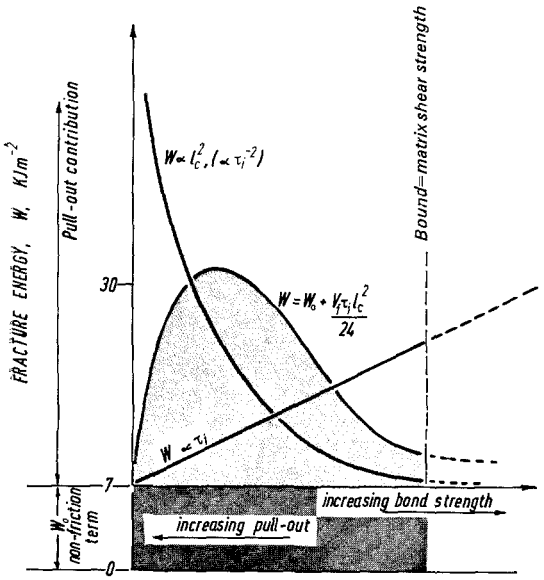

Figure 16 Schematic illustration of the variation of toughness with fibre/resin bond strength, τ_i, and critical length, l_c.

Outwater and Murphy suggest that if debonding does not occur ahead of a crack tip, the crack will pass undeviated through resin and matrix, and the resulting toughness will be a mixture-rule function of the toughnesses of fibre and matrix. For CFRP this would give a value of only about 100 J m^{-2}, compared with our estimate of about 7 K Jm^{-2}. The Outwater model could only apply, however, if the fibres were not bonded to the resin in the first place. In a real composite the stress distribution ahead of a crack tip is considerably more complex than in a homogeneous solid because of the mutual elastic constraints imposed on the fibre and resin by each other as a consequence of their different elastic moduli. As a crack travelling through a resin approaches a fibre, the stress concentration undergoes a discontinuous change at the interface (assuming continuity of strain) and a shear stress is developed in a somewhat similar manner to the way in which stress is transferred at the end of a fibre in a composite reinforced with short fibres. In addition to this longitudinal constraint there will, in well-bonded composites, be transverse elastic constraints in both fibres and matrix. These constraints could account for a considerable additional contribution to the overall fracture toughness as has been shown by experiments on metal laminates [22].

To some extent the necessity for these arguments is brought about by the low values of the fracture-energy of glass and carbon, both 5 to 10 J m^{-2}, that have been used in the rule-of-mixtures

calculation by Outwater and Murphy and by ourselves earlier. It has been assumed that the fracture energy of the fibre is the same as that of the bulk material, despite the great differences in the strengths of these materials in fibre and bulk form. It would be difficult to determine a proper "fracture toughness" value for a fibre only 8 μm in diameter, but we can nevertheless make an estimate of the stored elastic energy at failure and compare this with the stored elastic energy for tensile failure of a composite sample.

If we compare the processes of breaking a CFRP specimen in a tensile test and in a controlled bend test we can see that the stress/strain or load/deflexion curves will be quite different. The tensile curve will rise, usually linearly but with a few jerks as small groups of weak fibres give way here and there, until it reaches the specimen fracture stress. Failure is catastrophic and the load/deflexion trace falls to zero immediately. The rapid release of elastic energy stored in the machine does not permit a record to be obtained of the work of pulling-out the broken fibres. On the other hand, in the slow bend test the crack propagates more slowly and the load falls off gradually. The integrated curve gives the measured fracture toughness, including the frictional work, but the integrated tensile test curve gives only the work per unit volume of fracturing a brittle solid with strength σ_c and modulus E_c. It does not contain any frictional work. Since $\sigma_c = 0.7$ GN m^{-2} and $E_c = 144$ GN m^{-2}, the stored elastic energy per unit volume at fracture is

$$W_c = \tfrac{1}{2}(\sigma_c)^2/E_c \quad \text{J m}^{-3}$$
$$\sim 1.8 \times 10^6 \text{ J m}^{-3}$$

This is the work of initiating a crack plus the work of fracturing the brittle, orthotropic solid, but takes no account of any work done against friction in pulling out fibres. For a single type I carbon fibre $\sigma_f = 1.6$ GN m^{-2} and $E_f = 360$ GN m^{-2}, so that

$$W_f \approx 3.6 \times 10^6 \text{ J m}^{-3}.$$

On the basis of this result the composite with $V_f = 0.40$ should have a value of

$$W_c \sim 1.4 \times 10^6 \text{ J m}^{-2}.$$

We infer, then, that the fracture energy of the fibre material is much higher than that of the bulk; that a rule-of-mixtures sum gives adequately the major part of the fracture energy not contributed by pull-out; but that elastic constraints may also contribute slightly to this energy.

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