JOURNAL OF MATERIALS SCIENCE 28 (1993) 2238–2244

Study of the interface in Kevlar 49–epoxy composites by means of microbond and fragmentation tests: effects of materials and testing variables

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The work presented in the present paper focuses on the interface in Kevlar 49–epoxy composites. Experimental results for the interfacial shear strength obtained using the microbond test by means of different loading configurations (parallel plate loading, parallel conical plate loading, circular loading), are presented and compared. Contrasting with recent finite-element predictions proposed in the literature, the interfacial shear strength is found to be altogether insensitive to the type of microbond loading configuration. A comparison of the results obtained using two micromechanical tests (microbond and fragmentation) is performed. The interfacial shear strength results obtained by means of the fragmentation test are found to be higher by a factor of about 50% than those obtained by means of the microbond test. A possible explanation for this difference is proposed and discussed, and the value of the "true" interfacial shear strength is conjectured to fall between the values measured by these two tests. The effect of fibre surface chemistry modification (surface desizing) is probed by surface-sensitive techniques (XPS–ESCA and contact angle measurements from droplets) and by micromechanical testing techniques. Surface-sensitive techniques and micromechanical testing provide compatible information for the Kevlar–epoxy system studied here, and the knowledge of the chemical characteristics of the fibre surface can therefore be used as a means of predicting the interfacial shear strength.

1. Introduction

The microstructural features of the interface between a fibre and a matrix in a composite material are of critical importance in controlling the mechanical strength and toughness of the composite. The strength under shearing forces of the interface is viewed by most researchers as a key property since it reflects the ability of the composite to transfer stresses from an external mechanical field to the reinforcing phase (the fibre). Usually, stronger interfaces (or shorter stress transfer – or critical – fibre lengths) result in stronger, but more brittle, composite materials. The so-called "interfacial shear strength" can be measured using either macromechanical or micromechanical tests. Examples of macromechanical tests are the interlaminar shear strength test (ILSS) and the transverse tensile test. Such tests are usually simpler to conduct than micromechanical ones but in many cases it is doubtful whether a true fibre–matrix interfacial property is indeed measured. A number of micromechanical tests such as the fragmentation test, the pull-out test, the microindentation test, and the microbond test, have been used over the last few years and have been the subject of intensive research. This has culminated in an international round-robin exercise, the results of which were recently presented [1]. Micromechanical tests are very sensitive to changes in the interface chemistry and they are unambiguous regarding the failure mode (unlike macroscopic tests). One drawback is the fact that the specimens used are all (except the microindentation specimen) composite *model* configurations, wherein the stress state is quite different from that in a real-life composite. Another problematic aspect of both macroscopic and microscopic tests is the fact that all give different (albeit reproducible) values for the interfacial shear strength.

The work presented in the present paper has several purposes. First, microbond test results obtained using two different operators as well as different loading configurations are presented and compared. Second, a comparison of the results obtained for the interfacial shear strength using two micromechanical tests (microbond and fragmentation) is performed. Third, the effect of fibre surface chemistry modification (surface desizing) is probed by the surface-sensitive techniques of X-ray photoelectron spectroscopy (XPS) with electron spectroscopy for chemical analysis (ESCA) and contact angle measurements, and by micromechanical testing techniques. The objective of this was to determine whether surface-sensitive tech-

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niques and micromechanical testing would provide compatible information, and whether the knowledge of the chemical characteristics of the fibre surface might be used as a means of assessing (or predicting) the interfacial shear strength.

2. Experimental procedure

2.1. Materials

The fibre used in this study was Kevlar 49 poly(para phenylene terephthalamide) from Du Pont, with a nominal diameter of 11.9 μm. The filaments were used either in the as-received state, or desized by extraction for 4 h in a Soxhlet apparatus using toluene as a solvent. Desizing was followed by washing in acetone and drying under vacuum at 80 °C. The matrix material was DER 331 (Dow Chemical), a bisphenol A (DGEBA) based liquid epoxy resin with an average epoxy equivalent weight of 186–192, mixed with the curing agent DEH 26 tetraethylenepentamine (TEPA), with an amine equivalent weight of 27. The curing of the samples was performed according to the following schedule: 1 to 3 days at room temperature, followed by 3 h at 80 °C and 3 h at 100 °C, and final (slow) cooling. The resulting cured epoxy resin is a relatively stiff material, with Young's modulus, tensile strength and failure strain equal to 1.62 GPa, 55 MPa and 0.09, respectively.

2.2. Preparation of microbond specimens

Single filaments were carefully teased out from the fibre bundle and stretched horizontally on a frame using 2 g weights attached to the ends of each filament. Poxipol epoxy cement was then used to fasten the filament to the frame. Droplets of freshly prepared liquid epoxy were carefully spread on each filament using a boron fibre. The droplet length and thickness, and the fibre diameter, were measured after the curing was completed by optical microscopy. Finally, the fibre was cut on both sides of the droplet, and one side was used for tabbing using two roughened square aluminium tabs fastened with cyanoacrylate cement, leaving a 10 mm gauge length between the jaws of the tensile testing apparatus and the droplet. The dimensions of glycerol droplets spread on the fibres were used to calculate contact angle values using a recently developed algorithm [2] that is based on the work of Yamaki and Katayama [3] and Carroll [4].

2.3. Preparation of fragmentation specimens

The preparation procedure for the fragmentation specimens (prepared in the form of 100–200 μm films rather than the more common dog-bone specimens) was identical to that used in our previous work [5], to which the reader is referred.

2.4. Procedures for micromechanical tests

The microbond test has been described and analysed by various researchers since 1969 (see the literature review by Jiang and Penn [6]). Its principle is very simple, consisting of measuring the force necessary to debond the interface between a fibre and a solid droplet encasing it, by pulling the fibre in one direction and restraining the droplet in the opposite direction. Commonly, parallel knife-edges, yielding a two-point loading, are employed to restrain the droplet, although Haaksma and Cehelnik [7] and Andersson *et al.* [8] have performed their experiments using a circular area of contact (some finite-element work has also recently been initiated by Herrera-Franco and Drzal [9] to assess the possible difference in stress states between the point and circular loading configurations).

Here we performed a series of tests to assess the role of a few variables which we thought might have a strong effect on the pull-out data. First we analysed what would happen if two different operators performed identical tests (same material system, same testing procedure and apparatus). The tests were performed independently by two skilled, well-trained individuals, within a one-year interval. Significantly, these two individuals never had the opportunity to meet and exchange information, but rather they were given a list of instructions and procedures to follow. Second, we studied the effect of the geometry of the microbond loading system by performing three series of tests with parallel knife-edge loading (strictly, a two-point loading configuration), parallel cone–plate loading (also a two-point loading configuration), and circular loading (a uniform loading configuration). These loading configurations are illustrated in Fig. 1. For the parallel knife-edge configuration we used either 30 μm thick spacers (operator 1) or no spacers at all (operator 2); for the parallel cone–plate configuration we used no spacers; and for the circular loading configuration we used a small metallic disc containing a 30 μm circular hole. All microbond tests conducted with the Instron machine (parallel knife-edge and parallel cone–plate configurations) were performed at a deformation rate of 200 μm min^{-1}, whereas the tests conducted with our custom-made minitensile tester (circular loading configuration) were performed at a deformation rate of 30 μm min^{-1}.

We then performed a series of single-fibre composite (SFC, or fragmentation) tests with the same material systems, and a comparison between the results from these tests and those obtained from micropull-out tests was performed. The SFC tests were conducted using our custom-made minitensile tester at a deformation rate of 30 μm min^{-1}, and using a nominal gauge length of 20 mm. The average sample thickness was 150 μm and the test was continuously monitored by videomicroscopic means, as described in our previous publications [5, 10–13].

2.5. X-Ray photoelectron spectroscopy (XPS–ESCA)

The XPS studies of the as-received and desized Kevlar 49 fibres were performed using a PHI model 550 ESCA/SAM, using AlK_α radiation ($h\nu$ = 1486.6 eV) as an excitation source. The probing depth was estimated to be 10–30 atomic layers. To avoid peak shifts or

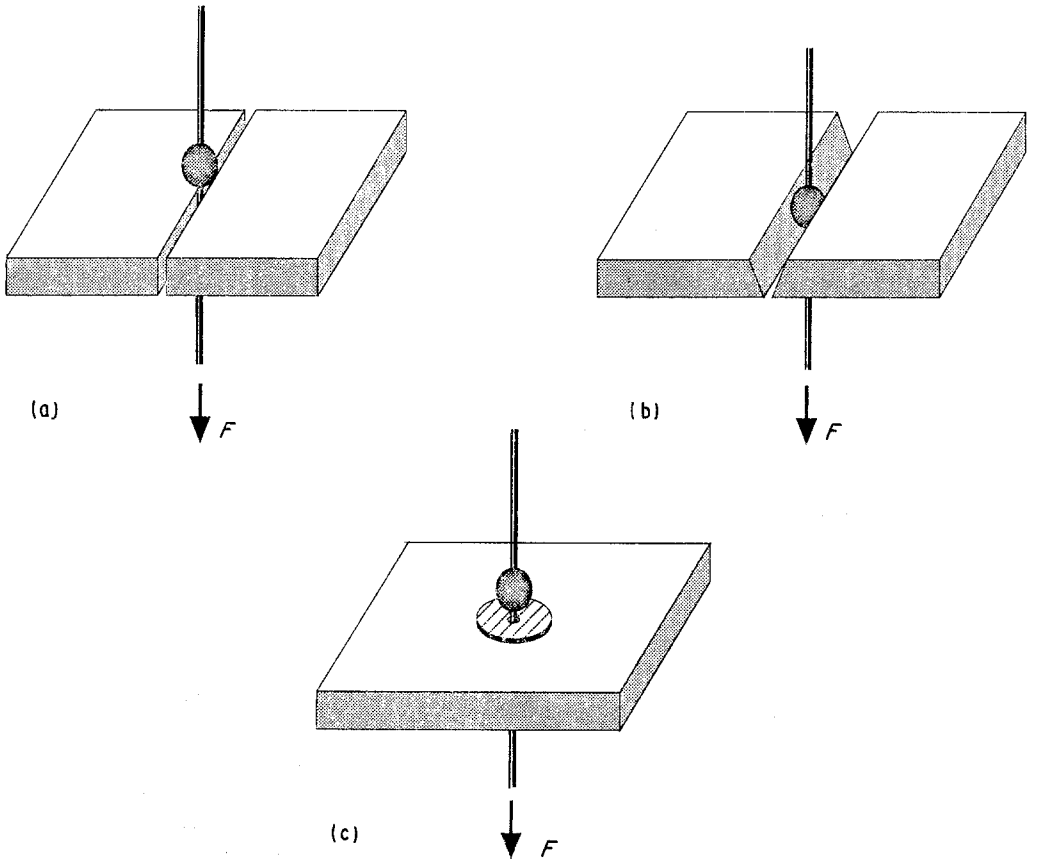

Figure 1 Geometries of the microbond loading system utilized in the present work: (a) parallel knife-edge loading (strictly, a two-point loading configuration), (b) parallel cone–plate loading (also a two-point loading configuration), and (c) circular loading (a uniform loading configuration).

distorsion due to sample charging, both sets of samples were exposed during the measurement to the same amount of electron flooding. The purpose of the XPS experiments was to determine whether the knowledge of the fibre surface chemical characteristics could be used as a means of assessing the interfacial shear strength.

2.6. Contact angle measurements

The difference in wettability characteristics between as-received and desized Kevlar 49 fibres was determined by means of contact angle measurements. This was performed by spreading small droplets of dry glycerol on the fibre specimen using a thin boron wire, and calculating the contact angle using a procedure described recently [2]. Assuming thermodynamic equilibrium and neglecting the effect of gravity, the reduced length L of the droplet on a cylindrical surface is given by [2–4]

$$L = 2[aF(\phi, k) + tE(\phi, k)] \quad (1)$$

where L = droplet length/cylinder radius, t = droplet half-thickness/cylinder radius and $a = (t\cos\theta - 1)/(t - \cos\theta)$ (refer to Fig. 2 where the contact angle θ is defined). F and E are Legendre's standard incomplete elliptic integrals of the first and second kind, respectively, which are tabulated. The arguments ϕ and k are calculated by using the expressions

$$k^2 = 1 - \frac{a^2}{t^2} \quad (2)$$

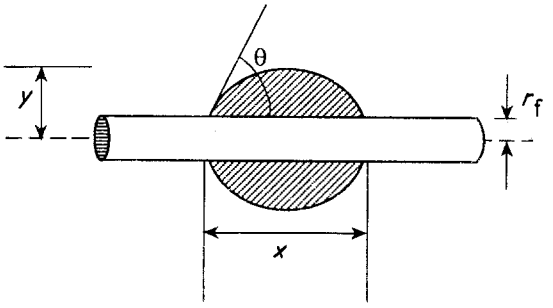

Figure 2 Contact angle θ formed by a liquid droplet on a cylindrical monofilament. Reduced droplet length $L = x/r_f$. Reduced droplet thickness $t = y/r_f$.

$$\sin\phi = \left[\frac{1}{k^2}\left(1 - \frac{1}{t^2}\right)\right]^{1/2} \quad (3)$$

As seen, the contact angle is not an explicit function of L and t and it is in fact not possible to invert Equation 1. An iterative solution was recently proposed by Wagner [2] in the form of a computer algorithm that uses an initial estimate of the contact angle θ, and the same algorithm was used here to obtain a fast and accurate value of the contact angle. This was also recently used by Gilbert *et al.* [14] for calculating the contact angle of glycerol on variously treated pitch-based carbon fibres, and by Tsai *et al.* [15] for calculating the contact angle of uncured liquid epoxy on Kevlar 29 fibres with various molecular chains attached at the fibre surface. If necessary, contact angle data may further be converted into surface energy values

using an equation-of-state approach, as in Gilbert *et al.* [14], but this was not pursued here.

Only symmetrical droplets were selected for measurement. The measurements were taken using a Leitz optical microscope, with magnifications of 400 for the droplet length and thickness and 1000 for the fibre diameter. A Colorado video micrometer (Model 305) was also used for some of these measurements. Similar to the XPS experiments, the purpose of the contact angle measurements was to determine whether the knowledge of the fibre surface wetting characteristics could be correlated with the interfacial mechanical shear strength.

3. Results and discussion

3.1. Micromechanical test results

Two methods were used to calculate the interfacial shear strength measured by means of the microbond test (whatever the loading configuration):

Method 1 (τ_1). The first and simplest way was to divide the debonding force F by the embedded area A (calculated from the measured embedded length) for each droplet tested. Thus for droplet i we calculated $\tau_i = F_i/A_i$, from which the average interfacial shear strength τ_1 was calculated as the arithmetic average of all τ_i values.

Method 2 (τ_2). The second way was to plot the debonding force F against the embedded area A and perform a linear regression through all data points pertaining to the rising region, leaving out those points which were judged (by simple optical inspection) to be part of the plateau region. These points were left out because Pitkethly and Doble [16] have recently argued that if the embedded length is too large the shear strength may be underestimated. Moreover, Penn and Lee [17] have advanced an argument concerning the inappropriateness of data at large embedded length. We also included the origin point (0, 0) in the linear regression, based on the fact that all theoretical models proposed in the literature [6] result in a line crossing the origin. This significantly increased the value of the coefficient of correlation. The slope of the regression line gave the interfacial shear strength estimate τ_2.

In Table I a comparison is made between the microbond results obtained by two independent operators using as-received Kevlar 49–epoxy specimens. As explained earlier, the tests were performed within a one-year interval by two skilled, well-trained individuals who never met or exchanged information. Both followed an identical list of testing instructions and procedures and, for this particular experiment, used the parallel knife-edge configuration with the Instron apparatus. The individual data are presented in Fig. 3a and b. From Table I it clearly appears that the

TABLE I Effect of operator on the measurement of the interfacial shear strength in Kevlar 49–epoxy by the microbond test

Operator	τ_1 (MPa)	Number of droplets	τ_2 (MPa)	Number of droplets
Operator 1	26.8	37	24.9	32
Operator 2	26.5	29	23.4	26

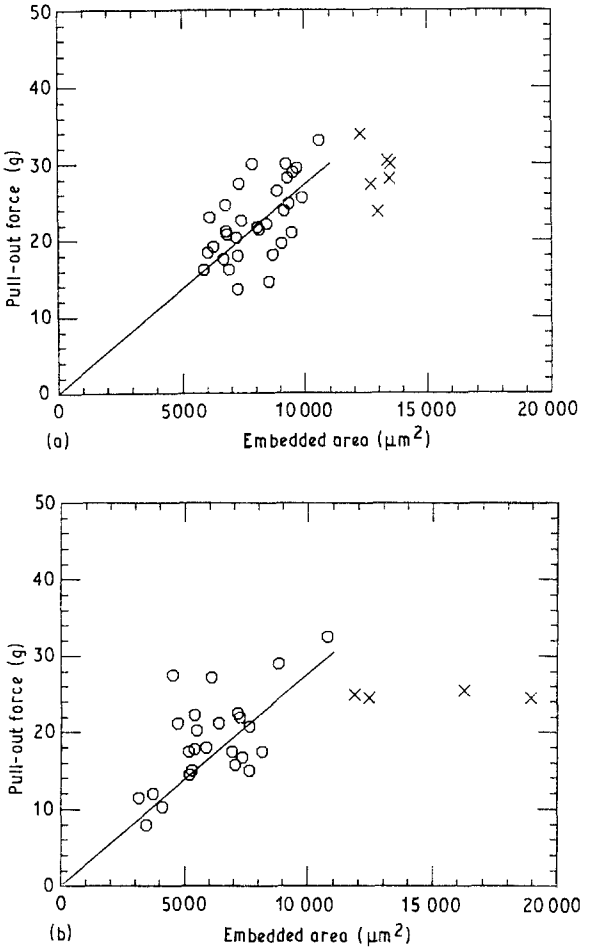

Figure 3 Microbond test data for as-received single Kevlar 49 filaments pulled out of an epoxy droplet, using parallel knife-edge loading: (a) operator 1, (b) operator 2. The regression line is through the data represented by open circles only.

TABLE II Effects of type of test, loading configuration and fibre surface chemistry on the interfacial shear strength of Kevlar 49–epoxy

Type of test	Loading configuration	Fibre surface	τ_2 (MPa)	Number of samples
Microbond	Parallel knife-edge (Instron)	As-received	24.9	32
		Desized	19.6	29
	Parallel cone–plate (Instron)	As-received	24.5	31
		Desized	–	–
	Circular hole (Minitester)	As-received	24.3	22
		Desized	19.7	22
Fragmentation	Minitester	As-received	32.6	5
		Desized	27.5	5

results are practically identical and therefore changing the operator does not represent a source of variability, provided the test is properly carried out.

In Table II the effects of the type of test (microbond versus fragmentation) and of the loading configuration (parallel knife-edge, parallel cone–plate and circular hole) on the microbond test results are shown, for both as-received and desized Kevlar 49 fibres in epoxy. The microbond test results presented are based on the data displayed in Figs 3–7. It is immediately apparent that, *regardless of the loading configuration*, the interfacial shear strength of as-received fibres in epoxy is about 24–25 MPa, and that of desized fibres in epoxy is about 20 MPa. This is a very significant result which contradicts claims by Haaksma and Cehelnik [7] that significant differences should exist between the parallel knife-edge and circular hole loading configurations. Note however that the epoxy system used here (and probably the cure conditions) is different from that used by them and it has been conjectured [18] that the microbond results would be much more sensitive to the loading configuration in the case of droplets made out of compliant epoxy matrices as compared to droplets made out of stiff epoxies (the DER 331–DEH 26 matrix system used here is a relatively stiff epoxy resin, according to its stress–strain curve and modulus, see details in Netravali *et al.* [19]).

An interesting point is raised by Herrera-Franco and Drzal [9] concerning the effect of loading configuration: interfacial shear stress distributions were obtained for different loading conditions by means of photoelastic and finite-element analyses, and it was noticed that differences as small as 4 μm in the relative position of the point of contact of the supports with the droplet might result in high differences in both the peak shear stresses and their location. This factor may be responsible, as claimed by Herrera-Franco and Drzal [9], for the high scatter usually observed with experimental microbond results. This argument is probably only partially correct. Indeed, it is true that in a typical experiment the spacing of the parallel knife-edges is always changed from specimen to specimen and adjusted to a gap wide enough to allow the fibre to move between them. Those differences in spacing result in differences in the relative point of contact and, consequently, induce changes in the state of stress at the fibre–matrix interface. However, we

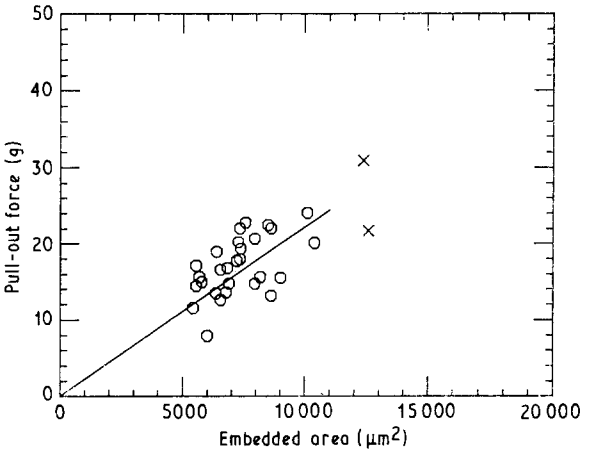

Figure 4 Microbond test data for desized single Kevlar 49 filaments pulled out of an epoxy droplet, using parallel knife-edge loading. The regression line is through the data represented by open circles only.

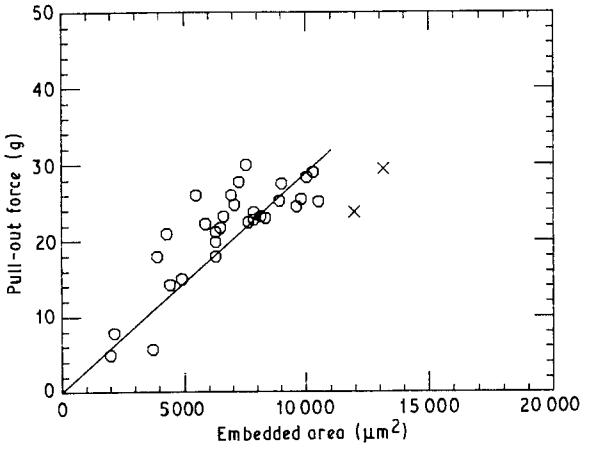

Figure 5 Microbond test data for as-received single Kevlar 49 filaments pulled out of an epoxy droplet, using parallel cone–plate loading. The regression line is through the data represented by open circles only.

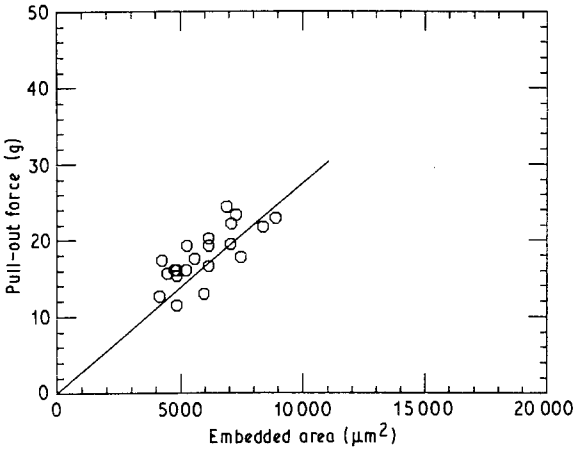

Figure 6 Microbond test data for as-received single Kevlar 49 filaments pulled out of an epoxy droplet, using circular hole loading.

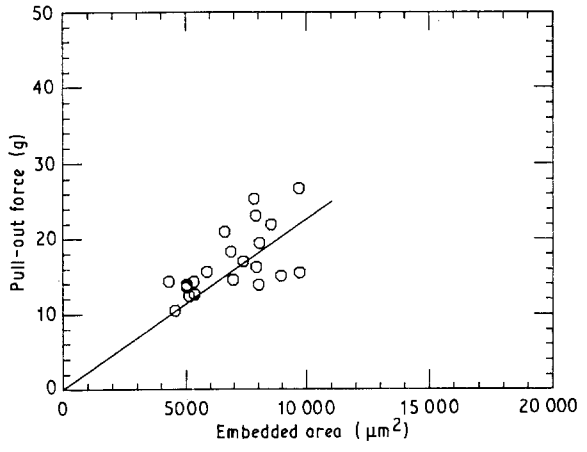

Figure 7 Microbond test data for desized single Kevlar 49 filaments pulled out of an epoxy droplet, using circular hole loading.

show in the present work that an equally high scatter is observed not only for the case just discussed (adjustable distance between the knife edges, corresponding to our experiment with parallel cone–plates) but also for the case where the spacing of the parallel knife edges is *not* changed from specimen to specimen (corresponding to our experiment with spacers between the edges), and for the case of circular loading with a constant hole diameter. This implies that there is more to the scatter than simply the effect of the loading configuration, but surprisingly enough the *average* interfacial shear strength is insensitive to the loading configuration. The only possible conclusion, therefore, is that the principal cause for this scatter is the inherent non-uniformity of the fibre surfaces, as already advanced by Penn and Lee [17] and Miller *et al.* [20].

The fragmentation data were analysed by means of the conventional Kelly–Tyson formula [21]:

$$\tau = 0.75 r_f \sigma_f(L_c)/L_c \quad (4)$$

where r_f is the fibre radius, L_c is the fibre critical length and $\sigma_f(L_c)$ is the strength of a fibre of length L_c. The latter was calculated using extrapolation data found in our previous work [22]. The fragmentation results presented in Table II show that the interfacial shear strength of as-received fibre–epoxy composites is higher than that of desized fibre–epoxy composites, as expected, but the values are higher than the corresponding values obtained from the microbond tests. Herrera-Franco and Drzal [9] (see their Table 3) obtain similar trends and explain these by claiming that the loss of curing agent in the small droplets (due to the large surface-to-volume ratio) generates mechanical properties that are slightly lower for the microdrops than for the matrix surrounding the single fibre in the fragmentation sample. Differences in the source of fracture energy for the failure events that take place for both tests are also advanced [9].

We would like to propose here another possible cause for the difference between the results of both tests, based on the fact that the fragmentation test tends to overestimate the interfacial shear strength results, whereas the microbond test tends to underestimate these. Indeed, for a given fibre–matrix system the fragmentation phenomenon is not observed (or is only partially observed, and includes debonding zones) unless a minimum bond strength is achieved at the interface. When testing such systems, only those samples that have a high enough interface shear strength will be accepted as valid samples, yielding an overestimation of the shear strength. When testing the same systems by means of the microbond method, only those samples in which the interfacial bond is not too large are measured since otherwise fibre breakage is obtained. Thus the fibres with a stronger interface are not sampled (this becomes even more critical when the embedded length is larger), resulting in an underestimation of the interfacial shear strength. Note that this also means that (a) the "true" or "absolute" value of the interfacial shear strength is never measured by these two techniques and (b) the "true" or "absolute" value of the interfacial shear strength is somewhere in between the values measured by the two techniques.

3.2. XPS and contact angle results

XPS spectra of as-received and desized Kevlar 49 fibres reveal the elemental peaks of carbon, oxygen and nitrogen, as well as traces of contaminants such as sodium, silicon, sulphur and chlorine (Table III). The surface of as-received fibres is richer in oxygen and poorer in nitrogen than the surface of desized fibres, which is expected since epoxy-compatible sizings usually are richer in oxygen-containing functional groups (such as C–O) than the fibres, and poorer in nitrogen-containing groups than the aramid fibres. Therefore, in view of the micromechanical results presented in the previous section, raising the concentration of oxygen-bearing functional groups improves the shear properties of the Kevlar 49–epoxy interface.

The contact angle between as-received or desized Kevlar 49 fibres and dry glycerol droplets was measured and calculated as explained earlier. The results are presented in Table IV. As seen, the average contact angle is significantly smaller in the case of as-received fibres than for desized fibres. It may therefore be concluded that a clear correlation seems to exist between the average contact angle using glycerol droplets, the surface oxygen concentration, and the interfacial shear strength, as illustrated in Figs 8 and 9.

TABLE III Contact angle determination from droplets of glycerol on Kevlar 49 filaments

Fibre	Average contact angle (deg)	Coefficient of variation (%)	Number of droplets
As-received	33.8	7.0	75
Desized	52.3	7.7	53

TABLE IV XPS results: elemental surface atomic percentages for as-received and desized Kevlar 49 filaments

Fibre	Surface atomic percentage						
	C	O	N	Si	Na	S	Cl
As-received	72.2	27.0	0.6	0.2	0.1	–	–
Desized	80.0	16.0	2.7	0.5	0.3	0.1	0.2

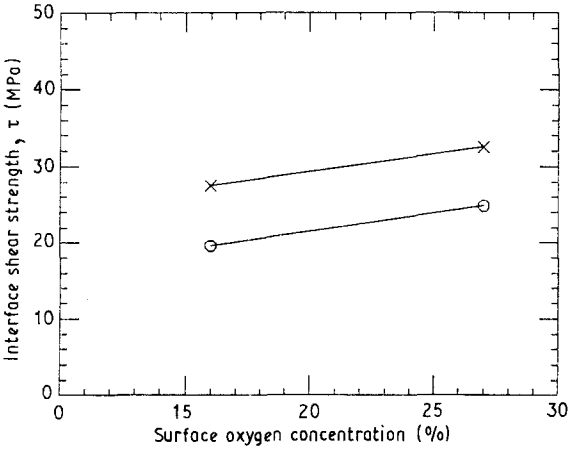

Figure 8 Correlation between the interface shear strength, measured by means of (×) fragmentation and (○) microbond tests, and the surface atomic oxygen concentration for as-received and desized Kevlar 49 fibres.

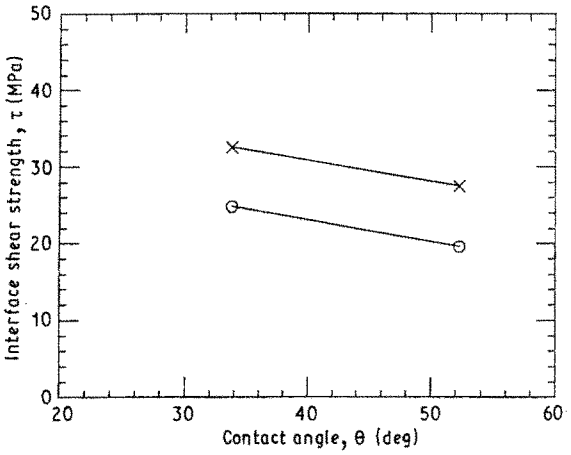

Figure 9 Correlation between the interface shear strength, measured by means of (×) fragmentation and (○) microbond tests, and the contact angle from a glycerol droplet for as-received and desized Kevlar 49 fibres.

Such correlation was recently observed for low-, medium-, and high-modulus pitch-based carbon fibres as well [14]. This finding demonstrates that the contact angle data using dry glycerol droplets on Kevlar 49 para-aramid fibres can be used directly to predict interfacial adhesive performance. This is by no means a universal result and such data have to be generated for each fibre–matrix system studied.

4. Conclusions

The major conclusions of the present experimental study may be stated as follows:

1. The interfacial shear strength of Kevlar 49–epoxy samples was measured by means of the microbond test using three different loading configurations, namely, parallel knife-edges, parallel conical edges, and circular hole. The interfacial shear strength was found to be altogether insensitive to the loading configuration.

2. It was demonstrated that the commonly observed wide interfacial strength data variability cannot be attributed to operator change: independent, well-trained operators produce statistically similar interfacial strength data.

3. The interfacial shear strength results obtained by means of the fragmentation test are higher by a factor of about 50% than those obtained by means of the microbond test. A possible explanation for this difference was proposed and discussed, and the value of the "true" interfacial shear strength was conjectured to fall between the values measured by these two tests.

4. A clear correlation seems to exist between the average contact angle using glycerol droplets on Kevlar 49 filaments, the surface atomic oxygen concentration, and the fibre–matrix interfacial shear strength. Contact angle data using dry glycerol droplets on Kevlar 49 para-aramid fibres can then be used directly to predict the interfacial adhesive performance of this fibre–matrix system.

Acknowledgement

This research was supported by a grant from the Philip M. Klutznick Fund for research at the Weizmann Institute of Science.

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Received 8 July
and accepted 11 August 1992