

Adhesive properties and failure of etched UHMW-PE fibres

M. S. SILVERSTEIN*, O. BREUER

Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

The effect of chemical etching on the surface of ultra-high molecular weight polyethylene (UHMW-PE) fibres with emphasis on the adhesion of epoxy to the fibres was studied. The presence of an oxygen-rich weak boundary layer on the non-polar UHMW-PE fibre yields poor adhesion for the as-received fibre and for fibres etched with the weaker etchants. A significant improvement in adhesion resulted when the weak boundary layer was removed and the UHMW-PE oxidized through etching with chromic acid, a stronger etchant. This significant improvement in adhesion was reflected not only in a higher interfacial shear strength but also in the presence of epoxy cohesive failure. The debonding of droplet microbonds was found to be a suitable technique for the characterization of adhesion in the UHMW-PE/epoxy system.

1. Introduction

1.1. Ultra-high molecular weight polyethylene fibres

Ultra-high molecular weight polyethylene (UHMW-PE) fibres are one of the more advanced polymer fibres in the high-performance fibre field [1]. The gel-spinning process yields a high degree of molecular orientation in these highly crystalline fibres [2]. A single fibre, tens of micrometres in diameter, is actually a composite of highly oriented submicrometre fibrillar strands [3]. The ultra-high specific strength, ultra-high specific modulus, and extraordinary impact resistance make them fibres of interest for advanced aerospace, military, automotive, and biomedical applications. The greatest drawback to using these fibres in composite material applications has been their poor adhesion to polymer matrices. Both the presence of a thin skin of low molecular weight fragments [3] and the non-polar UHMW-PE molecular structure yield poor adhesive properties.

1.2. Surface modification through etching

Several methods of fibre surface treatment including chemical etching have been used in an attempt to improve the properties of UHMW-PE fibre-reinforced composite materials [4]. The modification mechanism consists of the abstraction of hydrogen atoms from the polymer backbone and their replacement with polar groups. Polar groups on the fibre surface enhance wettability and present possible sites for chemical reactions with the matrix resin. The etching process not only changes surface chemistry but also surface morphology. An increase in surface roughness

can yield an increase in wetted area and can enhance adhesion through mechanical interlocking.

Chromic acid [5] and potassium permanganate [6] have been used as etchants for polyethylene. Chromic acid, potassium permanganate and hydrogen peroxide are the oxidants studied in this research. The fibre's surface composition, most importantly surface oxygen content, was characterized through a combination of electron spectroscopy for chemical analysis (ESCA) and Fourier transform-infrared spectroscopy (FTIR) [7]. A fibre flotation method was developed in order to estimate the effects of etching on fibre surface tension [8, 9]. The effects of etching on the single-fibre tensile properties were also investigated [3].

1.3. Adhesion in composite systems

The adhesion at the fibre-matrix interface is integral to composite mechanical properties [10]. Better stress transfer at the interface and a more efficient utilization of the system's composite nature can result from enhanced adhesion. The properties of the fibre surface directly affect the adhesion at the epoxy-fibre interface. Adhesion can be characterized through the debonding of an epoxy droplet microbond [11]. The droplet microbond is a variation of fibre microbond pull-out that can easily distinguish between shear debonding, droplet slippage and fibre breakage. This technique has been used successfully and reproducibly to determine the interfacial shear strengths of epoxy droplets on both glass and carbon fibres.

This paper will focus on the effects that chemical etching has on the adhesive properties of an UHMW-PE fibre/epoxy system. The relationships between

* Author to whom all correspondence should be addressed.

surface properties and adhesive properties will be discussed.

2. Experimental procedure

2.1. Materials

The UHMW-PE ($M_w = 1.5 \times 10^6$) fibre was a 120 filament Spectra-1000 tow of 650 denier (g/9000 m) from Allied Fiber Inc., VA. The chromic acid etching solution was prepared by mixing potassium dichromate (IV) ($K_2Cr_2O_7$), sulphuric acid (H_2SO_4) and distilled water in a 7:150:12 mass ratio. The potassium permanganate ($KMnO_4$) etching solution was prepared by mixing aqueous 0.2 M $KMnO_4$ and aqueous 0.2 M nitric acid (HNO_3) in a ratio of 4:1. The hydrogen peroxide (H_2O_2) etching solution was 30% H_2O_2 in water. The epoxy resin used for the microbond was Dow DER 324 with an equivalent epoxy weight of 190. The cure was effected for 24 h at room temperature by adding 10 wt % ethylene diamine to the epoxy.

2.2. Chemical etching

The fibres were separated from the tow and left in an etching solution at room temperature. The etching times were 5 min, 4 and 24 h. After etching, the fibres were first washed in running distilled water and then in ethanol. The fibres were dried in a vacuum oven at room temperature for 12 h.

2.3. Surface characterization

Surface oxygen content was measured through electron spectroscopy for chemical analysis (ESCA) with a resolution of 25 eV [7]. Fibres with a 50 nm gold coating were viewed in a scanning electron microscope (SEM) at 15 kV. Flotation curves were used to assess wettability. The probability of fibre flotation on various mixtures of *n*-propylamine and water yields a float-sink transition that can be ascribed to an apparent surface tension [9].

2.4. Droplet microbonds

Single fibres were taped to an aluminium frame in order to keep them taut. The mixture of epoxy and curing agent was applied to the taut fibres using another fibre. The application fibre was dipped in the epoxy and the droplet that formed at its tip was applied to the taut fibres under a stereo microscope. Two epoxy droplets between 100 and 600 μm diameter were applied to each fibre, with enough space between them to ensure that each droplet could be tested separately. The droplets were cured at room temperature for 24 h.

2.5. Droplet debonding

After the cure, the fibres were prepared for the debonding experiments. The fibres, both before and after droplet debonding, were examined in the optical microscope and SEM. The debonding was carried out

using the experimental jig illustrated schematically in Fig. 1, basically consisting of a calliper mounted on a base. The jig was attached to the crosshead of an Instron tensile testing machine. One end of the fibre was attached to the load-cell grip of the tensile testing machine. The free end of the fibre was passed through the centre of the jig such that the epoxy droplets lay below the gap in the crosshead. The calliper gap was then closed to a degree that just allowed the fibre to pass through freely.

The force needed to debond the epoxy droplet was measured with the fibre moving through the jig at a speed of 1 cm min^{-1} . The microbond area is taken as a cylinder formed by the fibre diameter and the length of fibre "embedded" in the droplet. The overestimation of the irregularly shaped fibre's diameter by microscopy should somewhat compensate for the perimeter-underestimating assumption of a cylindrical cross-section. The interfacial shear strength, τ_b , is defined as the debonding force divided by the microbond area. The interfacial shear strengths are averages of about 20 microbond experiments. The initial post-failure frictional stress is defined as the sliding force immediately after debonding divided by the microbond area.

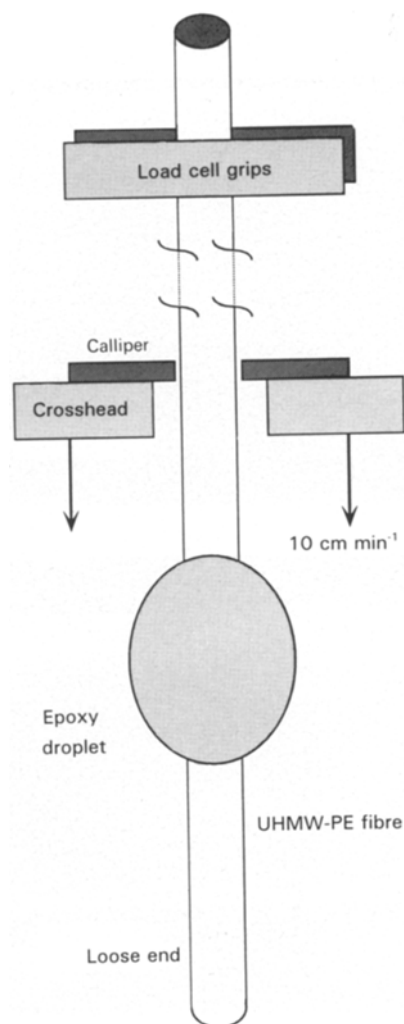


Figure 1 Schematic diagram of the debonding apparatus for an epoxy droplet/UHMW-PE fibre microbond.

3. Results and discussion

3.1. Surface structure

The etching process has both physical and chemical effects on the fibre surface. The changes in fibre surface roughness are seen in the electron micrographs in Fig. 2. The smooth surface in Fig. 2a is that of an as-received UHMW-PE fibre. The corrugated surface in Fig. 2b seen after etching with chromic acid for 4 h at room temperature reflects the fibrillar UHMW-PE fibre structure [3]. The skin layer on the as-received fibre is not as chemically resistant as UHMW-PE and is etched rapidly.

All the etchants remove enough of the skin layer to reveal fibrillar structures. The fibre structure after 4 h potassium permanganate etching is seen in Fig. 2c and after 4 h hydrogen peroxide etching in Fig. 2d. The fibrillar structure is most clearly defined in Fig. 2b. Chromic acid seems to be the more powerful etchant of the etchants studied.

3.2. Surface oxygen

The oxygen on the fibre surface (Table I) was characterized by ESCA for various fibre treatments [7]. There was 21.9% oxygen on the as-received fibre surface. Oxidized low molecular weight fragments and solvent excluded during crystallization can form the

oxygen-rich skin layer seen in Fig. 2. This oxygen-rich skin could not be removed by rinsing the fibre but was removed by etching. The significant amount of oxygen (13.5%) on the fibre surface after the skin was removed by chromic acid etching can be attributed to UHMW-PE oxidation.

Potassium permanganate and hydrogen peroxide were less powerful etchants than chromic acid. The potassium permanganate etching turned the fibres light brown while the other etchants had no discernible effect on fibre colour. There was a significant amount of oxygen (16.5%) and manganese (5.4%) on the fibre surface after 4 h in potassium permanganate. The particles on the potassium permanganate etched

TABLE I Surface oxygen content and apparent surface tension of UHMW-PE fibres

Etch	Time (h)	O (%)	γ_a (mN m ⁻¹)
None	–	21.9	32.9
Washed	–	22.2	–
K ₂ Cr ₂ O ₇	4	13.5	36.9
KMnO ₄	4	16.5 [5.4] ^a	36.5
H ₂ O ₂	4	6.6	30.4

^a [Mn, %]

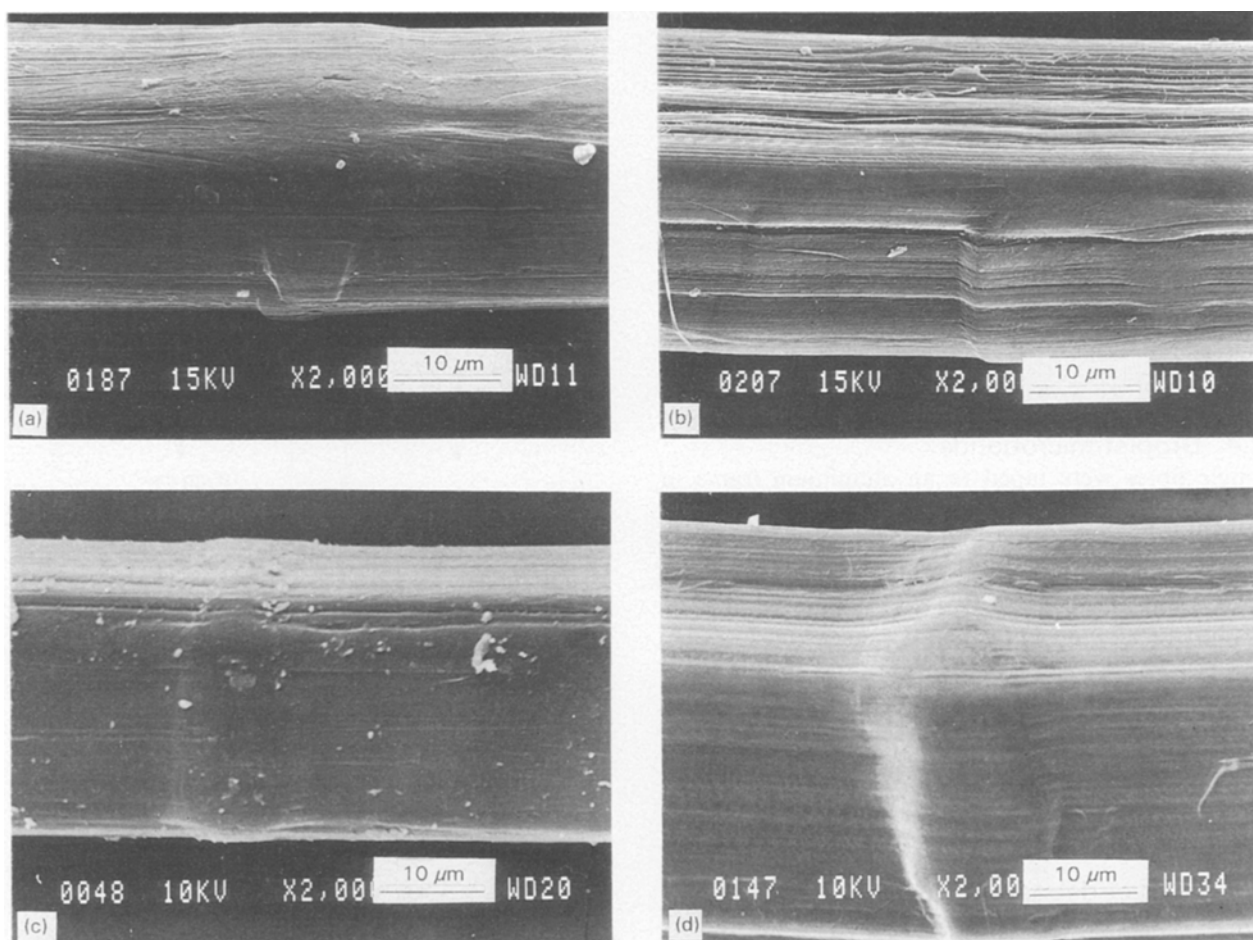


Figure 2 Scanning electron micrographs of fibres: (a) as-received; (b) after 4 h in chromic acid; (c) after 4 h in potassium permanganate; (d) after 4 h in hydrogen peroxide.

fibre surface in Fig. 2c could not be removed through vigorous rinsing. These particles seem to be manganese dioxide precipitated during the potassium permanganate etching process. These oxygen-rich precipitate particles account for most of the surface oxygen observed. The small amount of oxygen remaining that is associated with the fibre surface may be attributed to remnants of the skin layer. A similar small amount of oxygen on the 4 h hydrogen peroxide etched fibre surface (6.6%) may also be attributed to skin layer remnants.

3.3. Apparent surface tension

The wetting of the substrate is an important stage in adhesion. An increase in surface roughness is connected to an increase in apparent surface tension, and thus wettability, through the Wenzel equation [12]. An increase in polar groups on the surface also increases fibre wettability. A flotation method has been used to characterize the wettability of as-received and etched fibres [9]. An apparent surface tension, γ_a , based on fibre flotation, is listed in Table I for various surface treatments. This apparent surface tension should reflect both the effects of surface roughness and surface polarity on wettability. The apparent surface tension of the chromic acid-etched fibres is the largest while that of the hydrogen peroxide-etched fibres is the smallest.

3.4. Droplet debonding

The effects of surface treatment on adhesion were characterized through the debonding of epoxy droplet microbonds. The pre-debonding droplet seen in Fig. 3a for an as-received fibre is typical of all the fibres. The edge of the droplet in Fig. 3b (a higher magnification of Fig. 3a) seems to be well bonded to the fibre and there is no discernible gap between them. The definite post-debonding gap between fibre and droplet seen in Fig. 3c indicates adhesive failure.

Typical debonding interfacial shear stress curves are illustrated schematically in Fig. 4 for as-received and 4 h chromic acid-etched fibres. The two stress curves are quite similar in shape, but there is quite a significant difference in magnitude. The shape of the curve indicates that neither fibre breakage nor droplet deformation occur before droplet debonding [11]. The fibres did not break and the droplets did not slip before debonding throughout the debonding tests.

Interfacial shear strength data for as-received and chromic acid etched (4 and 24 h) fibres is seen in Fig. 5. There is no obvious dependence of interfacial shear strength on microbond area. The solid lines in Fig. 5 represent the average interfacial shear strengths. The debonding reveals two groups of epoxy droplet microbonds, strongly bonded ($\tau_b > 3$ MPa) and weakly bonded ($\tau_b < 3$ MPa). The interfacial shear strengths for different fibre treatments are listed in Table II.

The as-received fibres are weakly bonded. The interfacial shear strength for the as-received fibres is 1.7 MPa. This weak bonding might not reflect epoxy adhesive failure at the epoxy interface as the epoxy

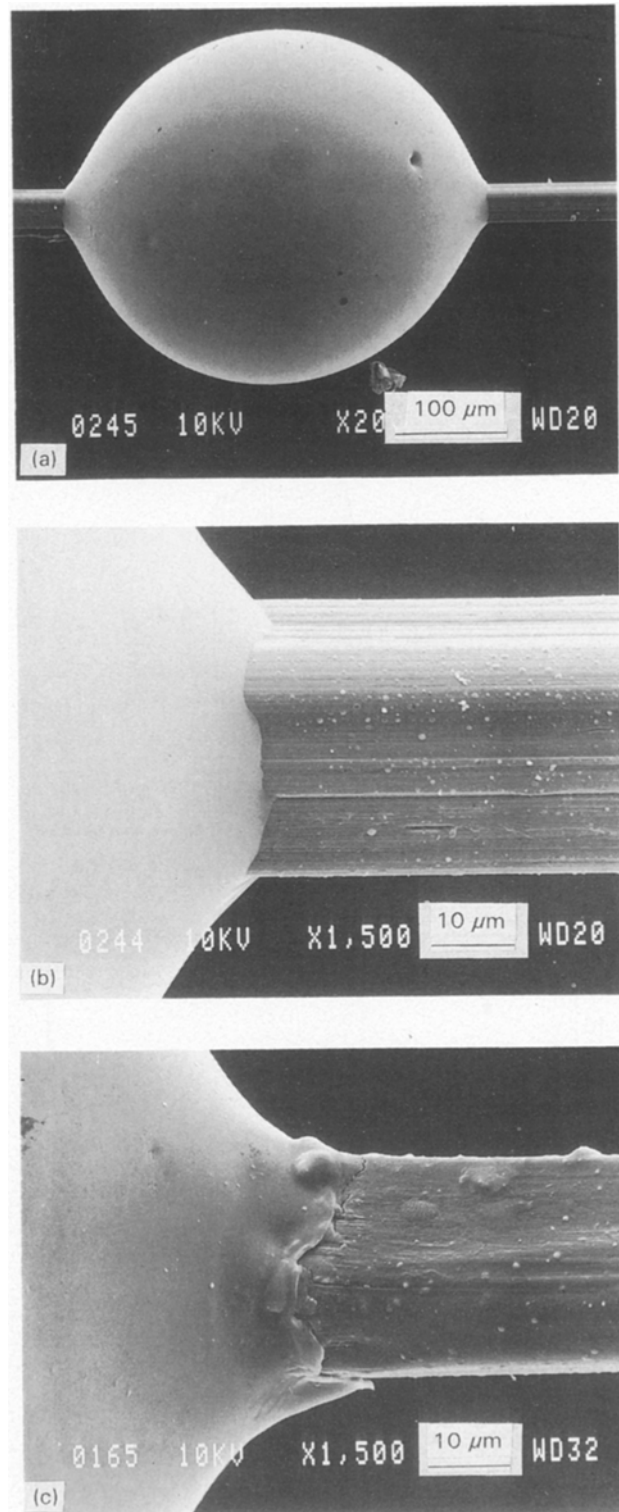


Figure 3 Scanning electron micrographs of cured epoxy droplet on fibres: (a) before debonding; (b) before debonding (higher magnification); (c) after debonding.

may actually be adhering strongly to the skin. The adhesive failure may occur instead between the skin and UHMW-PE. The skin acts as a weak boundary layer limiting the adhesive properties. The standard deviation of 53% in strength is quite large and may be in part related to poor equipment sensitivity at low debonding forces.

The potassium permanganate and hydrogen peroxide-etched fibres are also weakly bonded. The manganese dioxide precipitate particles seen in Fig. 2c are

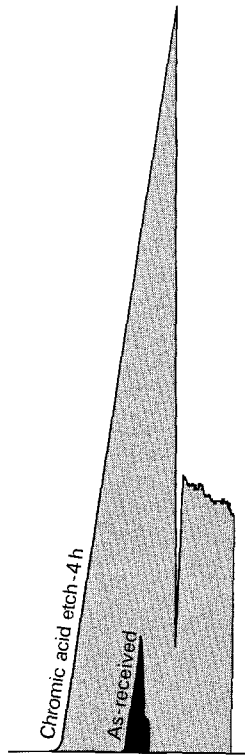


Figure 4 Typical debonding interfacial shear stress curves for an epoxy droplet on an as-received fibre and on a fibre etched for 4 h in chromic acid.

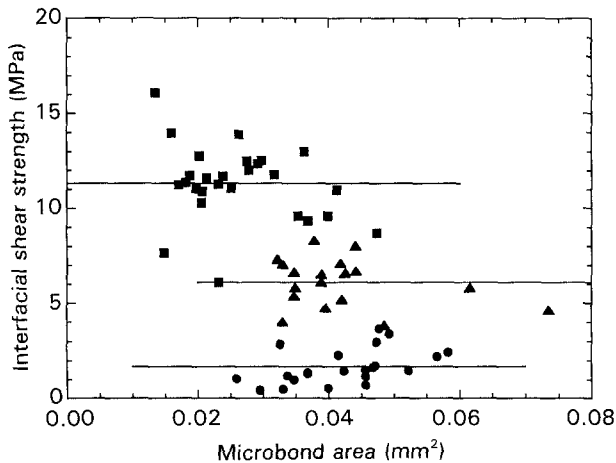


Figure 5 Interfacial shear strength data for epoxy droplets on UHMW-PE fibres: (●) as-received; (■) after 4 h in chromic acid; (▲) after 24 h in chromic acid.

TABLE II Interfacial shear strength of epoxy droplets on UHMW-PE fibres

Etch	Time (h)	τ_b (MPa)
None	—	1.7 ± 0.9
$K_2Cr_2O_7$	4	11.3 ± 2.0
	24	6.1 ± 1.2
$KMnO_4$	4	3.2 ± 1.0
	24	2.4 ± 1.0
H_2O_2	4	1.3 ± 0.8

not seen on the post-debonding fibre surface in Fig. 6a. The particles seem to have been embedded in and strongly bonded to the epoxy. The particles, like a weak boundary layer, are pulled off the fibre with the epoxy droplet during adhesive failure. The combination of a weak boundary layer and the non-polar UHMW-PE yields poor adhesion.

The fibres etched in chromic acid are strongly bonded. This strong bonding occurs directly between the epoxy and the UHMW-PE because the weak boundary layer has been removed by etching. The interfacial shear strength of the 4 h chromic acid etched fibres is 11.3 MPa, more than six-fold that of the as-received fibres. These interfacial shear strengths are of the same order of magnitude as the interlaminar shear strengths found for an UHMW-PE fibre-reinforced epoxy composite in flexure [13]. The interfacial shear strength of the strongly bonded UHMW-PE fibres is still significantly less than those of glass and carbon fibres [11].

The standard deviations for both weakly and strongly bonded fibres lie between 1 and 2 MPa. The standard deviation of 18% in strength for the fibres etched 4 h in chromic acid reflects not only improved equipment sensitivity at higher debonding

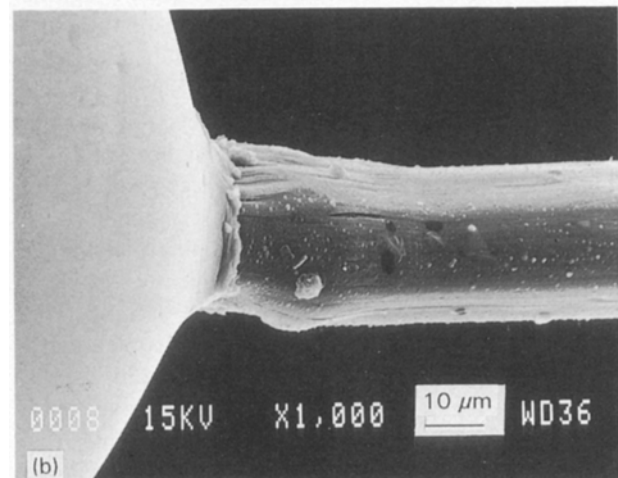
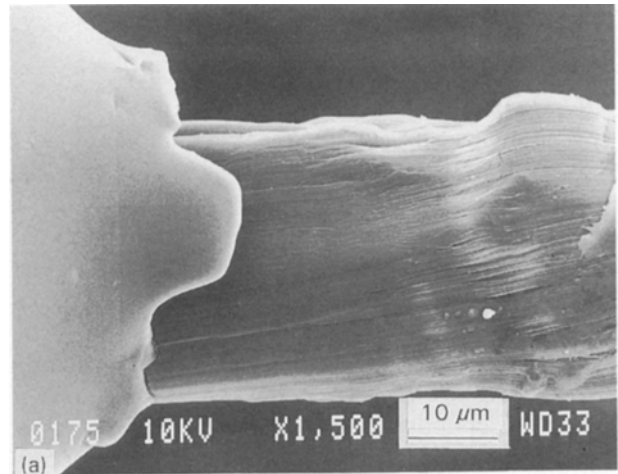


Figure 6 Scanning electron micrographs of droplet edge after debonding on fibres: (a) after 4 h in potassium permanganate; (b) after 4 h in chromic acid.

forces but also the greater reliability of the bonds. The Weibull distribution in Fig. 7 for the fibres from Fig. 5 shows that the UHMW-PE/epoxy bond reliability increases with increasing interfacial shear strength. The Weibull modulus, an indicator of statistical reliability, increases from 1.8 for the weakly bonded as-received fibres to 5.6 for the strongly bonded 4 h chromic acid-etched fibres.

The debonding force should be linearly proportional to microbond area. The force does seem to increase linearly with microbond area for the as-received, 4 and 24 h chromic acid-etched fibres in Fig. 8. The lines in Fig. 8 are generated by taking a least-squares fit to the data points. The extrapolated data should pass through the origin and do pass close to the origin for the strongly bonded fibres. The extrapolation through the as-received fibre data, typical of the weakly bonded fibres, falls relatively far from the origin.

The interfacial shear strength was derived assuming a failure mechanism of uniform yielding at the interface along the length of the fibre. An alternative failure mechanism is one governed by an energy criterion. According to this criterion the failure occurs when the

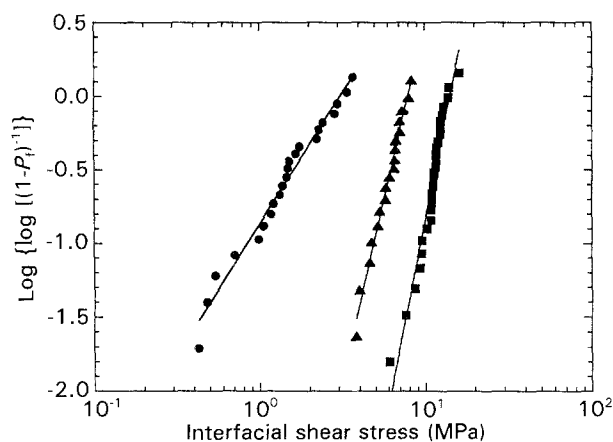


Figure 7 Weibull distribution of interfacial shear strength data for epoxy droplets on UHMW-PE fibres: (●) as-received; (■) after 4 h in chromic acid; (▲) after 24 h in chromic acid.

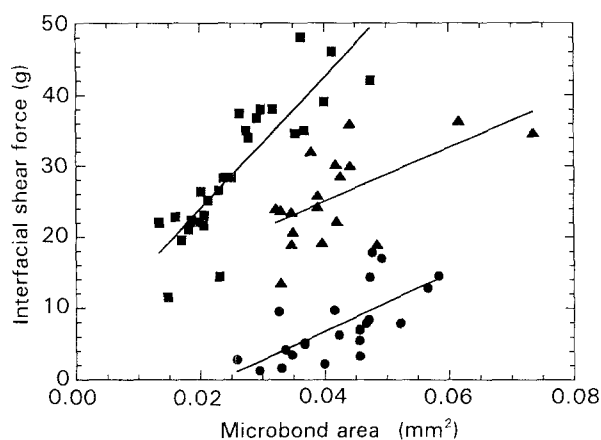


Figure 8 Interfacial shear force data for epoxy droplets on UHMW-PE fibres: (●) as-received; (■) after 4 h in chromic acid; (▲) after 24 h in chromic acid.

energy supplied to the system exceeds the energy needed for debonding [14]. A third failure mechanism describes the progressive failure of the bond starting from the points of maximum stress at the fibre ends [15]. All three failure mechanisms predict linear relationships between debonding force and droplet geometry that have an intercept at the origin. All three models yield non-origin intercepts for the weakly bonded UHMW-PE fibre/epoxy systems. This non-origin intercept seems to indicate that the area covered by the droplet is significantly greater than the actual bonded area.

3.5. Post-failure sliding

The post-debonding behaviour of droplet microbonds is also of interest. The epoxy droplets slide along the UHMW-PE fibre with an associated frictional stress after debonding. The stress curve for epoxy on the as-received fibre in Fig. 4 exhibits a post-debonding frictional stress of 0.5 MPa. The 4 MPa post-debonding frictional stress for epoxy on the 4 h chromic acid-etched fibres is significantly greater. These differences in the post-debonding behaviour are related to the type of debonding failure.

A smooth post-debonding fibre surface typical of the weakly bonded fibres is observed in Fig. 6a for a potassium permanganate etched fibre. The removal of the precipitate particles indicates a weak boundary layer type of debonding failure. There is no indication of epoxy cohesive failure. The low frictional stress reflects the small coefficient of friction for epoxy on highly oriented UHMW-PE.

There are particles of epoxy adhering to the fibre surface after droplet debonding on chromic acid-etched fibres in Fig. 6b. The failure process is a combination of interfacial adhesive failure and epoxy cohesive failure. The change from pure adhesive failure originates in the significant improvement in epoxy/UHMW-PE adhesion. The adhering epoxy particles create a rough epoxy-studded surface with a significantly greater coefficient of friction. The frictional force needed to pull the epoxy-coated fibre through the epoxy droplet after debonding becomes significantly greater.

3.6. Adhesion enhancement

The changes in fibre surface properties with chromic acid etching yield important changes in the adhesion mechanisms. The surface properties of the as-received and 4 h-etched fibres are presented in Fig. 9. The overall surface oxygen content, apparent surface tension, and interfacial shear strength are each normalized by their maximum value in Fig. 9. No direct relationship can be derived from this comparison of surface properties and adhesion. The characterization of the epoxy/UHMW-PE system must take into account not only surface roughness and surface oxygen but also the contribution of a weak boundary layer, etching precipitates, and polymer oxidation to the bonding and failure processes.

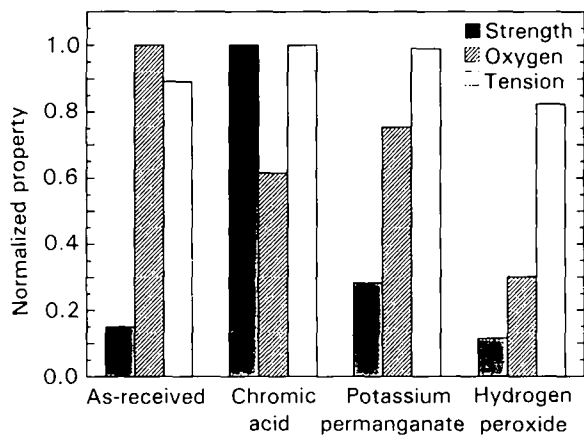


Figure 9 Normalized properties from Tables I and II: surface oxygen content (± 21.9 at %); surface tension (± 36.9 mN m⁻¹); interfacial shear strength (± 11.3 MPa).

4. Conclusions

The as-received, potassium permanganate- and hydrogen peroxide-etched fibres are all weakly bonded to epoxy. The poor adhesion reflects the presence of an oxygen-rich weak boundary layer on the non-polar UHMW-PE. Chromic acid, the more powerful of the etchants studied, can remove the weak boundary layer and oxidize the UHMW-PE. The enhanced adhesion of the chromic acid-etched fibres is reflected in the more than six-fold improvement in interfacial shear strength to 11.3 MPa and in the epoxy cohesive fail-

ure. The adhesive properties are influenced by a complex relationship between surface structure, surface polarity, and surface roughness.

References

1. S. BORMAN, *Chem. Eng. News* 9 October (1989) 23.
2. P. J. BARHAM and A. KELLER, *J. Mater. Sci.* **20** (1985) 2281.
3. M. S. SILVERSTEIN and O. BREUER, *ibid.*, in press.
4. B. TISSINGTON, G. POLLARD and I. M. WARD, *ibid.* **26** (1991) 82.
5. D. BRIGGS, D. M. BREWIS and M. B. KONIECZO, *ibid.* **11** (1976) 1270.
6. R. H. OLLEY, A. M. HODGE and D. C. BASSET, *J. Polym. Sci. Polym. Phys. Ed.* **17** (1979) 627.
7. M. S. SILVERSTEIN, O. BREUER, and H. DODIUK, in preparation.
8. A. MARMUR, W. CHEN, and G. ZOGRAFI, *J. Coll. Interface Sci.* **113** (1986) 114.
9. M. S. SILVERSTEIN and O. BREUER, *Polymer*, in press.
10. I. E. NIELSEN, in "Mechanical Properties of Polymers and Composites", Vol. 2 (Marcel Dekker, New York, 1974) p. 471.
11. B. MILLER, P. MURI and I. REBENFELD, *Compos. Sci. Technol.* **28** (1987) 17.
12. A. J. KINLOCH, "Adhesion and Adhesives" (Chapman and Hall, New York, 1987) p. 23.
13. B. TISSINGTON, G. POLLARD and I. M. WARD, *J. Mater. Sci.* **26** (1991) 82.
14. M. R. PIGGOTT, *Compos. Sci. Technol.* **30** (1987) 295.
15. P. LAWRENCE, *J. Mater. Sci.* **7** (1972) 1.

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