

# Surface Modification of UHMWPE Fibers

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## SYNOPSIS

Ultrahigh molecular weight polyethylene (UHMWPE) fibers have a high specific strength, high specific modulus, and outstanding toughness, but their poor adhesive properties has limited their use for composite material applications. In this research, the effects of chemical etching on the surface chemistry and topography have been explored using chromic acid, potassium permanganate, and hydrogen peroxide etching. The smooth surface observed on the as-received fiber was rich in ether and/or hydroxyl oxygen. This smooth surface resulted from the presence of an outer layer, a weak boundary layer, that was removed by all the etchants. A fibrillar structural hierarchy was revealed beneath this outer layer and the fiber was relatively unchanged by further etching. Chromic acid, the strongest etchant studied, produced a rough and oxidized UHMWPE surface with both ether and carbonyl oxygen. The combination of outer layer removal, roughness, and changes in oxygen bonding helps explain the improved adhesion on chromic acid etching in spite of the reduction in surface oxygen. Neither hydrogen peroxide nor potassium permanganate etching roughened or oxidized the surface to a great extent and neither yielded improved adhesion. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

### UHMWPE Fibers

Ultrahigh molecular weight polyethylene (UHMWPE) fibers have many properties that are advantageous for lightweight composite materials.<sup>1</sup> A high degree of molecular orientation from the gel spinning process yields a high specific strength, high specific modulus, and outstanding toughness.<sup>2</sup> The extraordinary chemical resistance, wear resistance, low coefficient of friction, and biocompatibility ensures that these fibers are of interest for advanced aerospace, military, automotive, and biomedical applications. The poor adhesion of these fibers to polymer matrices has been a limiting factor in their use for composite material applications. Chemical etching and plasma etching have both been used in an attempt to improve the adhesion between UHMWPE fibers and epoxy.<sup>3</sup>

### Surface Treatment

The power of the etchant and the specific changes to the surface introduced by etching determine the resulting degree of adhesion enhancement.<sup>4</sup> The etching mechanism seems to consist of the abstraction of hydrogen atoms from the polymer backbone and their replacement with polar groups. The polar groups introduced on the fiber surface should increase the surface tension and enhance wetting. One of the more significant changes in the fiber's surface chemistry is the introduction of carbon-oxygen bonds. These polar groups increase surface tension, enhance wetting, and present possible sites for chemical reactions with an epoxy resin yielding enhanced adhesion.

The etching process often roughens the surface. The Wenzel equation predicts that an increase in surface roughness will yield an increase in surface tension and enhanced wetting.<sup>5</sup> The increase in roughness also presents sites for mechanical interlocking between an epoxy matrix and the fiber. The effects of chemical etching on the single fiber mechanical properties,<sup>6</sup> wetting,<sup>7</sup> and adhesion to

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epoxy<sup>4</sup> have been investigated. This article explores the changes in surface topography and surface chemistry on etching that are basic to an understanding of the changes in other properties.

## EXPERIMENTAL

### Materials

The UHMWPE ( $M_w = 1.5 \times 10^6$ ) fiber was a 120 filament Spectra-1000 tow of 650 denier (gram per 9000 meter) from Allied Fiber Inc., Virginia. The chromic acid (CA) etching solution was prepared by mixing potassium dichromate (IV) ( $K_2Cr_2O_7$ ), sulfuric acid ( $H_2SO_4$ ), and distilled water in a 7 : 150 : 12 mass ratio. The potassium permanganate (PP,  $KMnO_4$ ) etching solution was prepared by mixing aqueous 0.2M  $KMnO_4$  with aqueous 0.2M nitric acid ( $HNO_3$ ) in a 4 : 1 ratio. The hydrogen peroxide (HP,  $H_2O_2$ ) etching solution was 30%  $H_2O_2$  in water.

The fibers were separated from the tow and without washing or pretreatment placed in the etching solution at room temperature. The etching times were 5 min, 4 h, and 24 h. After etching, the fibers were first washed in running distilled water for 2 min and then in running ethanol for 2 min. The rinsing process was also applied to untreated as-received (AR) fibers. The fibers were dried in a vacuum oven at room temperature for 12 h.

### Surface Characterization

Fibers with a 50 nm gold coating were viewed in a JEOL JSM-840 scanning electron microscope (SEM) at 15 kV. The fibers were arranged on a standard sample holder with double-sided tape for standard SEM analysis. X-ray microanalysis was performed in the SEM using energy-dispersive spectroscopy (EDS). For EDS analysis, a slot was cut out of the center of the sample holder to prevent the holder from contributing to the EDS spectrum. The fibers that were stretched over the slot in the holder were analyzed using EDS.

The surface oxygen content was measured through electron spectroscopy for chemical analysis (ESCA). A Perkin-Elmer Physical Electronics 555 ESCA/Auger with an  $AlK\alpha$  X-ray source and an energy of 25 eV for high resolution was used. The fibers were taped to an aluminum film and a 40° angle of incidence used. The overall spectrum was taken at low resolution and the spectra of elements of interest were taken at high resolution.

Several spectra were deconvoluted to more accurately describe the contributions of different bonds to the overall peak. Prior to deconvolution, the background was subtracted from the spectrum using one iteration of the Shirley method.<sup>8</sup> The total spectrum is described by the sum of mixed Gaussian/Lorentzian functions, each representing a particular spectrum peak. An individual spectrum is described by eq. (1).<sup>8</sup> The peak heights ( $p$ ) of each spectrum were readily solved by a curve-fit program given the known binding energy at the peak ( $x_0$ ) and assuming a consistent shape for all the spectra. This shape is set by keeping two parameters constant: (a)  $\beta$ , which is approximately one-half the full-width at half-maximum (fwhm), and (b)  $M$ , the tendency for the spectrum to be Lorentzian (where  $M = 0$  describes a Gaussian spectrum and  $M = 1$  describes a Lorentzian spectrum). From curve-fitting spectra with minimal oxygen, the C1s spectrum peak shape was described by setting  $M = 0.7$  and  $\beta = 1 \pm 0.15$ . The carbon-carbon peak was taken to be -285 eV with a -1.5 eV shift for every carbon-oxygen bond:

$$f(x) = \frac{p}{\{1 + M[(x - x_0)/\beta]^2\} \times \exp\{[1 - M][\ln(2)][(x - x_0)/\beta]^2\}} \quad (1)$$

A Nicolet 50× Fourier transform infrared (FTIR) spectrometer was used in transmission using a microscope to locate the beam. The IR spectra from 4000 to 400  $cm^{-1}$  were characterized. The ratio of peaks representing different functional groups were compared to the C—C peak at 1469  $cm^{-1}$ . Peaks representing ether, carbonyl, and carboxyl were taken at 1110, 1740, and 2640  $cm^{-1}$ , respectively.

## RESULTS AND DISCUSSION

### As-received Fibers

#### Surface Texture

The as-received (AR) UHMWPE fiber surface has a smooth relatively featureless surface (Fig. 1) with an irregular ellipsoidal cross section. The fiber profiles observed in both optical and electron microscopy indicate that the fibers can be described by a "diameter" that varies between 20 and 30  $\mu m$ . The irregularity in the surface is the result of ridges 2–5  $\mu m$  peak to peak running parallel to the fiber length. Bulges 5–10  $\mu m$  in length that merge smoothly with the surface are commonly found along

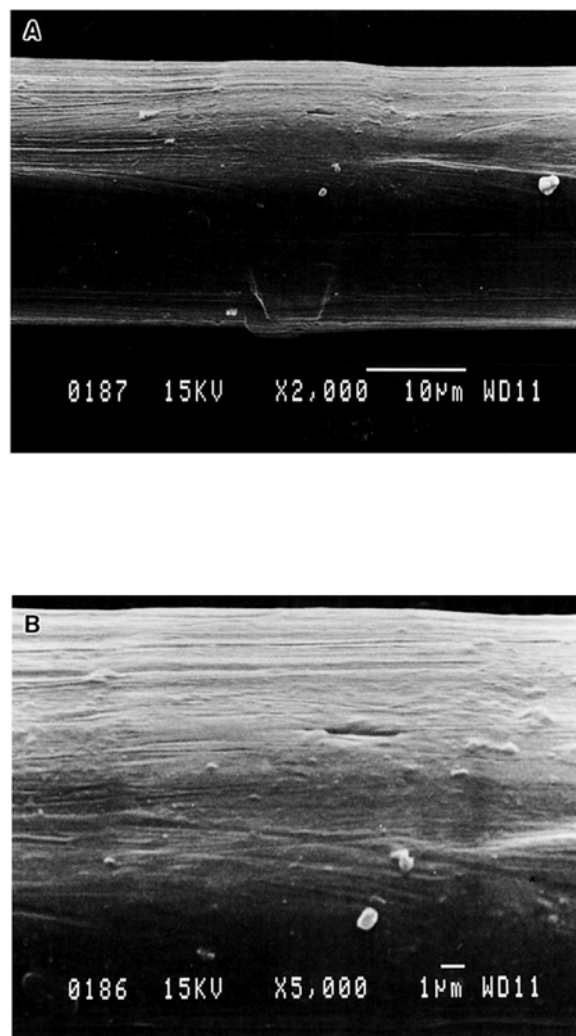


Figure 1 SEM micrographs of AR fiber.

the length of the fiber. These bulges are kink bands that have formed on the fiber surface during processing and handling.<sup>9</sup>

#### Surface Chemistry

The 22% oxygen on the fiber surface in Table I from ESCA analysis seems to originate in oxidized spinning oils and low molecular weight fragments excluded during crystallization.<sup>10</sup> The C1s spectrum in Figure 2(a) results from subtracting the background from the original data. Both the original data and the removed background are represented in the figure. The C1s spectrum exhibits a larger area to the left of the peak than to the right of the peak. The bulk of the additional area seems to originate in the spectrum for a single carbon-oxygen bond with a peak at  $-286.5$  eV.

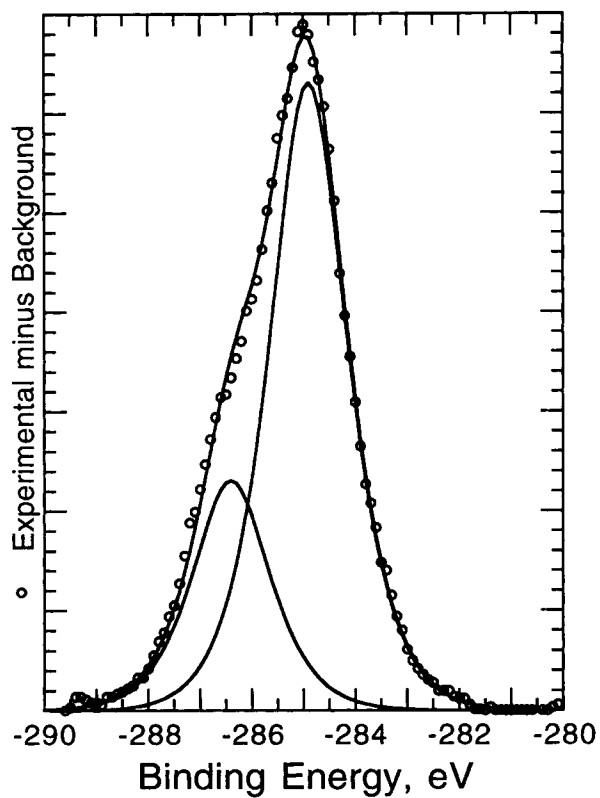
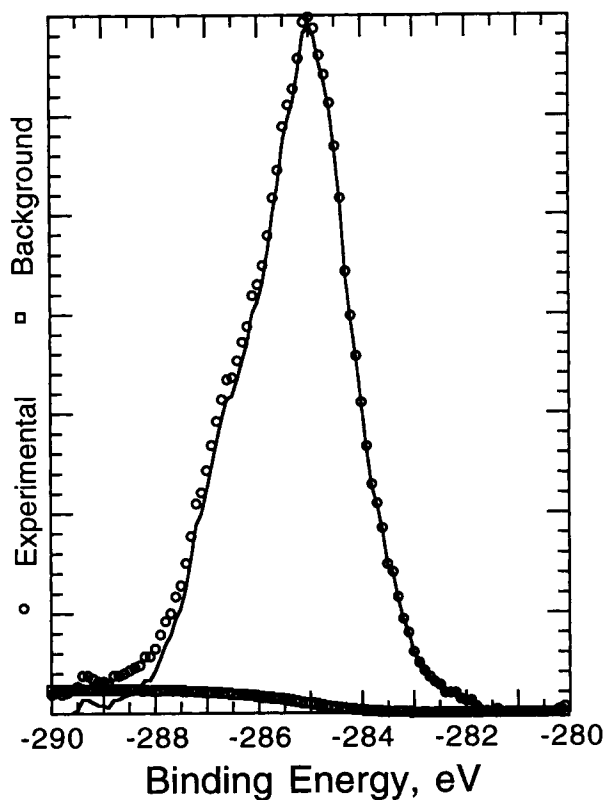


Figure 2 ESCA spectra of AR fiber: (a) C1s (background removed); (b) C1s (background removed, deconvoluted).

**Table I** Elemental Analysis of Fiber Surface from ESCA

Surface Treatment	C (at %)	O (at %)	Mn (at %)	Si (at %)	Other (at %)
<b>AR</b>					
Untouched	74.2	21.9	0.0	2.8	1.1
Ethanol	73.0	22.2	0.0	3.1	1.7
<b>CA</b>					
5 min	89.6	9.4	0.0	0.8	0.2
4 h	84.2	13.5	0.0	0.0	2.3
24 h	87.9	8.9	0.0	1.6	1.6
<b>PP</b>					
4 h	73.6	16.5	5.4	0.0	4.5
24 h	62.5	23.4	13.0	0.0	1.1
<b>HP</b>					
4 h	91.6	6.6	0.0	0.0	1.8

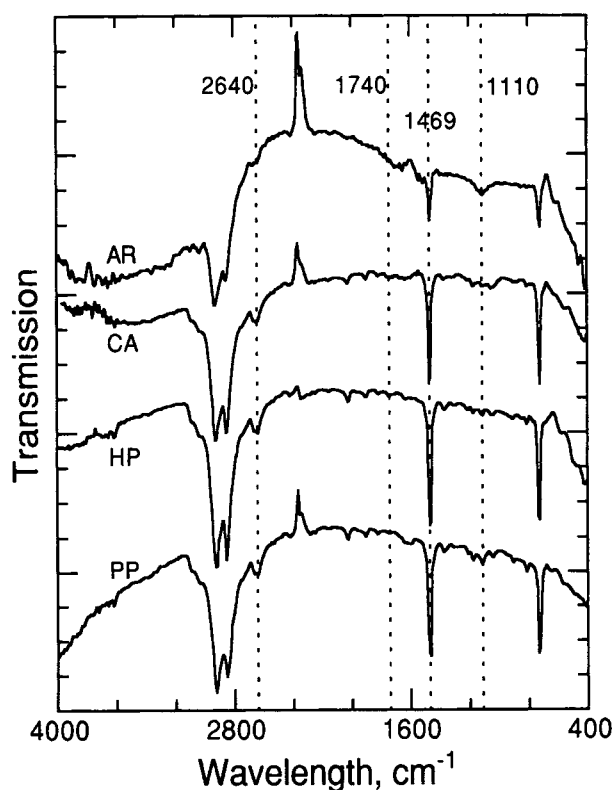
This C1s spectrum with the background removed was deconvoluted into contributions from peaks at  $-285$  and  $-286.5$  eV in Figure 2(b). The overall spectrum in Figure 2(b) is the sum of the two component peaks shown and fits the C1s spectrum quite well. The bulk of the oxygen seems to be bonded to the carbon in the form of hydroxyl or ether. The contribution of the area of the spectrum whose peak is at  $-286.5$  to the overall area is 27%. A very small maximum at  $-289.5$  eV, corresponding to carbon bonded thrice to oxygen, is observed. Its signal, however, is within the noise level and so its contribution was not included in this discussion. Carbon twice bonded to oxygen, whose peak would be located at  $-288$  eV, exhibited no significant contribution to the C1s spectrum. The O1s spectrum is significantly noisier than the C1s spectrum and its deconvolution would not yield accurate results.

It was expected that rinsing the fibers in ethanol would remove the oxygen-rich surface layer.<sup>10</sup> The 22% oxygen on the ethanol-rinsed fiber surface in Table I, however, indicates that the oxygen content was not significantly changed by the rinsing. The C1s and O1s spectra of the rinsed fibers were similar to those of the AR fibers. In addition, the smooth surface profile of the fibers (Fig. 1) that reflects the presence of this layer was unaltered by rinsing.

The presence of oxygen on the fiber surface is also reflected in the FTIR profile in Figure 3. The FTIR technique was not particularly surface-sensitive and the signal from the surface was somewhat overwhelmed by the signal from the bulk. In spite of this lack of surface sensitivity, there were several typical carbon-oxygen group peaks in the spectrum.

These peaks provide another indication of the significant oxygen presence on the fiber surface.

The ratio of functional group peak heights to the height of the PE peak at  $1469$   $\text{cm}^{-1}$  are presented in Table II. The large peak at  $1110$   $\text{cm}^{-1}$  in Fig-

**Figure 3** FTIR spectra of AR and etched fibers.

**Table II Functional Group Peak Ratios from FTIR**

	$\frac{h(1110)}{h(1469)}$	$\frac{h(1740)}{h(1469)}$	$\frac{h(2640)}{h(1469)}$
AR	0.33	0.07	0.21
AR, rinsed	0.21	0.05	0.16
CA, 4 h	0.10	0.04	0.16
PP, 4 h	0.14	0.02	0.16
HP, 4 h	0.06	0.03	0.17

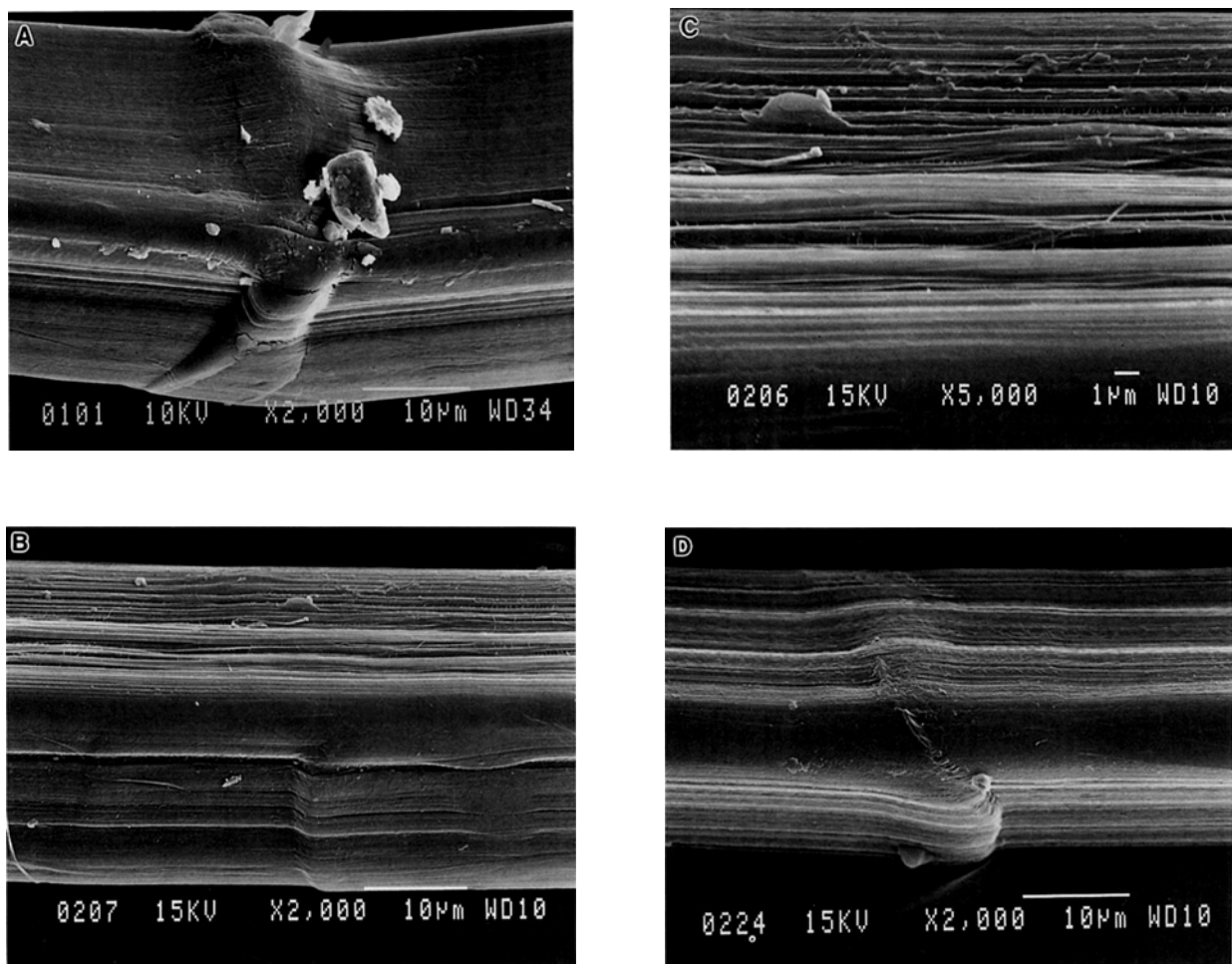
ure 3 indicates the overwhelming presence of ether groups on the fiber surface with a peak ratio of 0.33. There is a smaller contribution to the spectrum from carboxyl groups ( $2640\text{ cm}^{-1}$ ) with a peak ratio of 0.21. There is a much smaller contribution from carbonyl groups ( $1740\text{ cm}^{-1}$ ) with a peak ratio of 0.07. The FTIR spectrum confirms the conclusions

drawn from the ESCA analysis: The AR fiber has an oxygen-rich surface in which the single oxygen-carbon bond is dominant. Rinsing in ethanol does not substantially remove the oxygen groups from the fiber surface. The ether group's peak ratio is somewhat reduced by rinsing in ethanol, as seen in Table II. The carbonyl and carboxyl groups' peak ratios are only slightly reduced.

### Chromic Acid Etching

#### Surface Texture

Etching 5 min in CA substantially changes the topography of the fiber surface (Fig. 4). The shape of the ridges and bulges on the fiber surface are more clearly distinguished. At high magnification, the fibrillar nature of the UHMWPE fibers becomes discernible, especially at the edge of a kink band. The lines running parallel to the fiber length that were



**Figure 4** SEM micrographs of CA etched fibers: (a) 5 min; (b, c) 4 h; (d) 24 h.

barely visible on the as-received fiber surface are more highly defined.

After 4 h etching, the highly oriented fibrillar structure becomes quite obvious. The fiber surface has a corrugated structure. The ridges observed previously are the contours of bundles of submicron fibrils. These fibrils are on the order of 100 nm in diameter and are highly oriented in the direction of the fiber length. The fibrils are interconnected by smaller fibrils, nanofibrils, on the order of 10 nm in diameter (Fig. 4). Etching 4 h in CA yields a significant improvement in the wetting of the fibers<sup>7</sup> and in the adhesion to the fibers (Table III).<sup>4</sup> The rough fibrillar surface remains relatively unaltered with further etching. There was no significant decrease in fiber diameter with etching, even after 24 h.

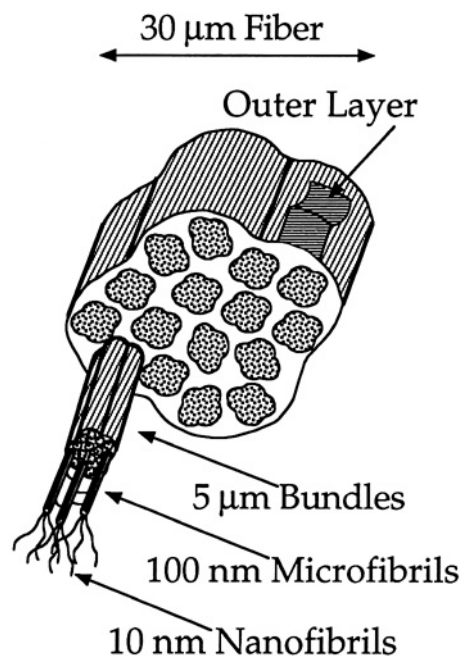
The surface of the AR fiber is sensitive to the etchant with significant topographical changes resulting after 5 min. Once this surface layer has been removed, however, the UHMWPE beneath exhibits resistance to etching. The etchant sensitivity of the smooth AR fiber surface confirms the presence of a distinct surface layer that is not etchant-resistant UHMWPE. Removal of this layer by etching improves the adhesive properties.<sup>4</sup> The outer layer thus acts as a weak boundary layer, yielding poor adhesive properties. The fibrillar structural hierarchy and the thin outer layer revealed through etching is described by the schematic illustration in Figure 5.

### Surface Chemistry

The ESCA results in Table I reflect the removal of an oxygen-rich outer layer from the fiber surface. The oxygen on the fiber surface is reduced from 22% to 9% through etching in CA for 5 min. The C1s spectra for the fiber etched 5 min in Figure 6 is considerably more symmetrical than that for the AR

**Table III Interfacial Shear Strength of Epoxy Droplet Microbonds**

Fiber		$\tau_b$ (MPa)
AR	—	$1.7 \pm 0.9$
CA	4 h	$11.3 \pm 2.0$
	24 h	$6.1 \pm 1.2$
PP	4 h	$3.2 \pm 1.0$
	24 h	$2.4 \pm 1.0$
HP	4 h	$1.3 \pm 0.8$

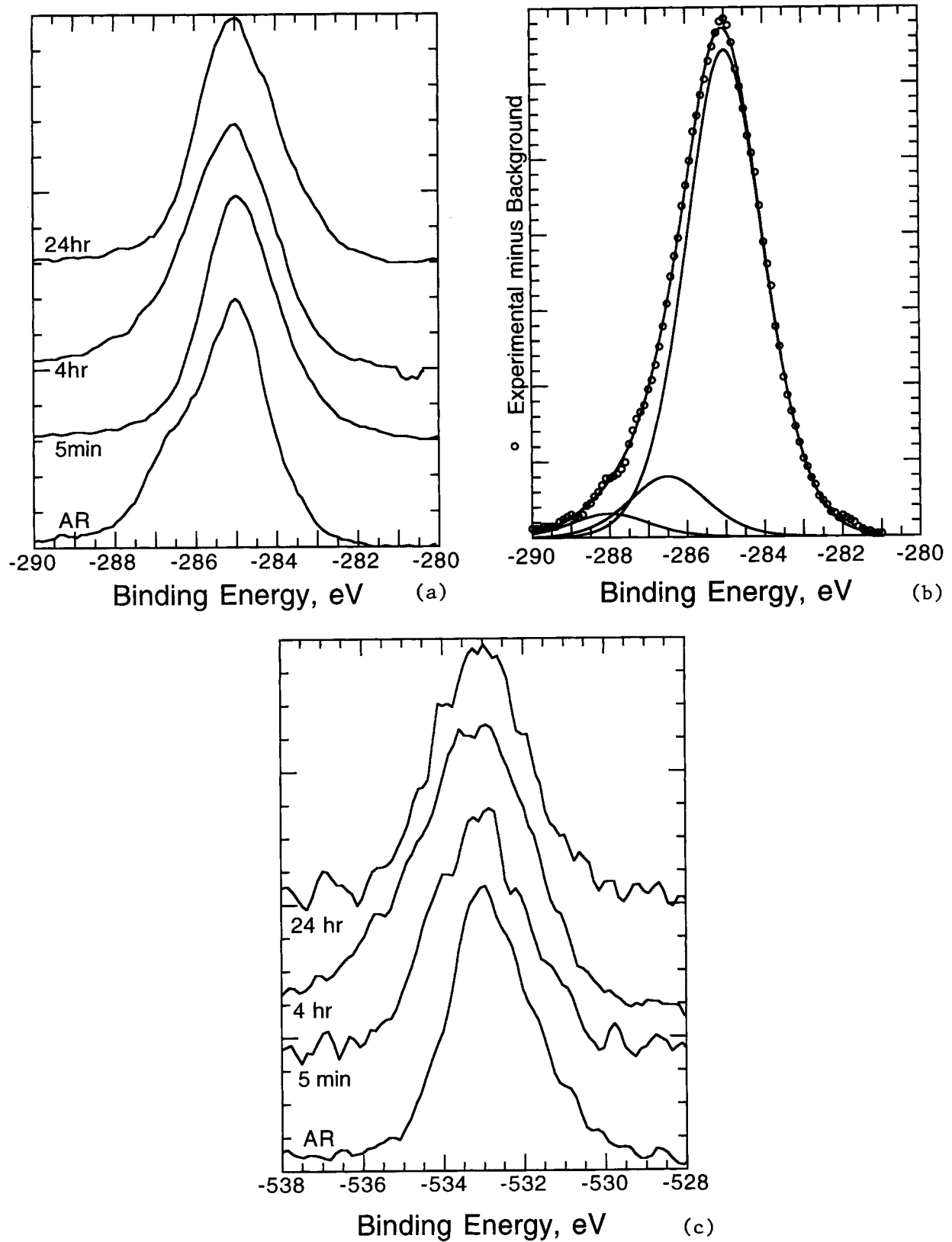


**Figure 5** Schematic illustration of UHMWPE fiber's structural hierarchy.

fiber, reflecting a reduction in the contributions from carbon–oxygen bonds. The continuation of the etching process, however, yields an increase in oxygen content to 14% (Table I) and a broadening of the C1s peak (Fig. 6). This increase in oxygen content might represent the etching of amorphous UHMWPE revealed on the surface through the removal of the outer layer.

Deconvolution of the C1s peak for a fiber etched 4 h in CA in Figure 6(b) shows that there is now a significant contribution both from carbon bonded once to oxygen and from carbon bonded twice to oxygen with peaks at  $-286.5$  and  $-288$  eV, respectively. The area of the spectrum whose peak is at  $-286.5$  eV contributes 12% to the overall area, whereas that at  $-288$  eV contributes 2%. The removal of the outer layer, roughening of the surface, and introduction of functional groups to the UHMWPE help to explain the significant improvement in interfacial shear strength between the etched fiber and epoxy.<sup>4</sup> Further etching reduces the oxygen content and yields a more symmetric C1s peak (Fig. 6). This reduction in oxygen content is accompanied by a reduction in adhesive strength<sup>4</sup> and may reflect the removal of oxidized UHMWPE from the fiber surface and fiber embrittlement.<sup>6</sup>

The O1s spectra in Figure 6 for the etched fibers were noisier than those of the AR fibers and even more difficult to deconvolute into their component



**Figure 6** ESCA spectra of CA etched fibers: (a) C1s; (b) C1s of fiber etched 4 h (background removed, deconvoluted); (c) O1s.

peaks. The O1s spectra of these etched fibers were significantly broader than those of the AR fibers, indicating a large variety of bonds with oxygen and confirming the deconvolution of the C1s spectrum that indicated the rise in the contribution of carbon bonded twice to oxygen.

The decrease in elemental oxygen and the change from an overwhelming preponderance of a single carbon-oxygen bond in relationship to other carbon-oxygen groups are also seen in the FTIR spectra in Figure 3. The peak ratios in Table II indicate a significant decrease in ether groups on the fiber surface, from 0.33 in the AR fibers to 0.10 in the fibers etched for 4 h in CA. The peak ratio for carbonyl and carboxyl bonds have decreased slightly. This confirms the decrease in oxygen content seen in ESCA. The large decrease in the ether contribution increases the relative significance of the carbonyl contribution. This confirms the relative increase in significance of the carbon bonded twice to oxygen in the deconvoluted ESCA C1s spectrum of the fibers etched 4 h in CA in Figure 6(b).

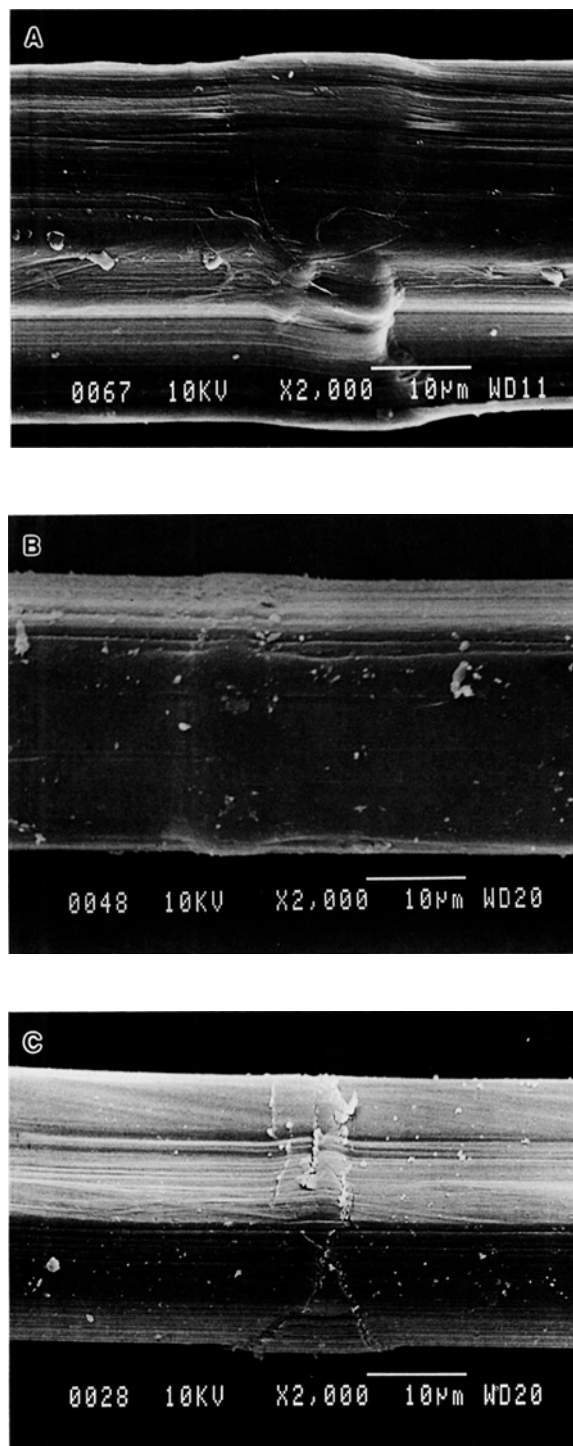
### Potassium Permanganate Etching

#### Surface Texture

The PP etching reveals the same fibrillar surface in Figure 7 as seen in CA etched fibers (Fig. 4). The fibrils oriented along the fiber length are observed after 5 min etching and the shapes of the kink bands are more highly defined. Further etching produces a slight increase in the definition of the fibrillar shape, but not to the extent seen with CA etching. The particles that appear on the fiber surface were not observed on either the AR- or CA-etched surfaces. The number and size of these particles, the result of the formation of an etching byproduct, increases with etching time. PP is the only etchant that significantly changed the color of the fibers. The etched fibers turned brown and this discoloration could not be removed through vigorous rinsing.

#### Surface Chemistry

The EDS spectrum (not shown) of the fibers at low magnification revealed the presence of Mn. In contrast, Cr, K, or S were not found in EDS or ESCA of CA etched fibers. EDS spectra were also taken at high magnification both for a single particle and for a particle-free area of the fiber. The particle exhibited a high concentration of Mn, whereas the particle-free area exhibited a lower concentration of Mn. The brown color of these tightly bound Mn-rich particles seems to be typical of manganese ox-



**Figure 7** SEM of PP etched fibers: (a) 5 min; (b) 4 h; (c) 24 h.

ides that range from MnO to MnO<sub>2</sub>, the most likely byproduct.<sup>11</sup>

The ESCA spectrum confirms the results of EDS in Table I. There is 5.4% Mn after 4 h etching and



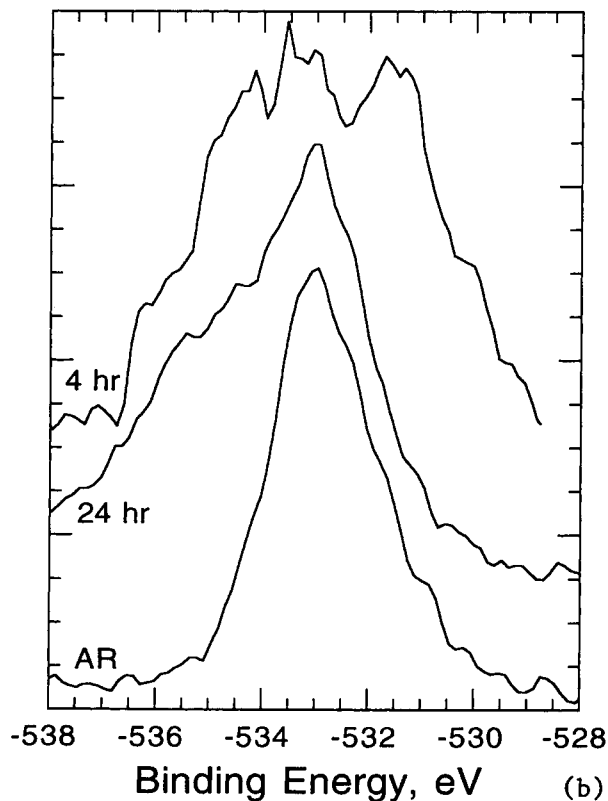
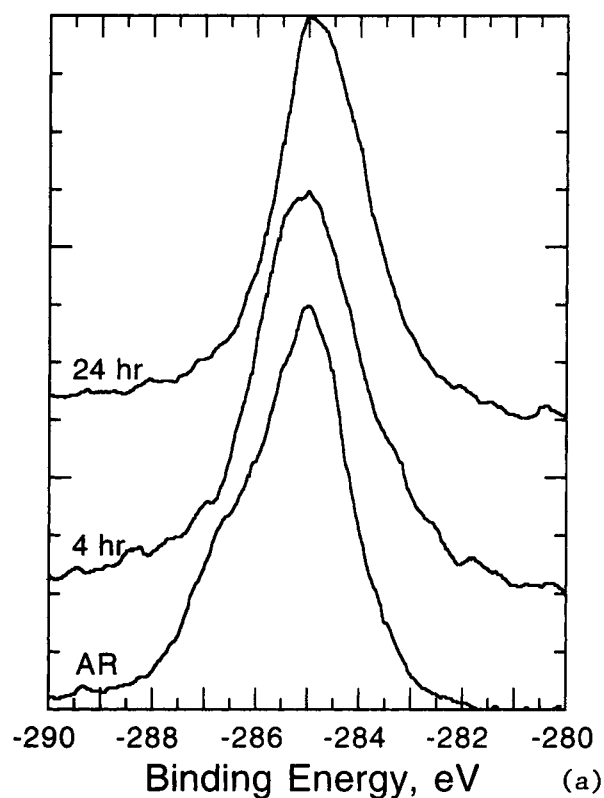
13% Mn after 24 h etching. The formation of a manganese oxide etching byproduct would account for a great deal of the oxygen observed on the fiber surface. The amount of oxygen actually bonded to the polymer after etching in PP could be quite low. The influence of carbon–oxygen bonds on the shape of the relatively symmetric C1s spectrum in Figure 8(a) for a fiber etched 24 h in PP with 23% oxygen on its surface seems relatively small. The relatively broad O1s spectra in Figure 8(b) reflects a range of bonds with oxygen. The narrow C1s spectra and broad O1s spectra indicate that there is a significant amount of oxygen that is bonding with manganese and not with carbon.

The ether peak ratio from the FTIR spectra in Figure 3 is reduced from 0.33 for the AR fibers to 0.14 for the fibers etched 4 h in PP in Table II. The carbonyl and carboxy peaks are slightly reduced by PP etching. This reduction in peak ratios is similar to that seen for the CA-etched fibers. The precipitates on the surface and the lack of UHMWPE oxidation helps explain the insignificant effect of PP etching on adhesion (Table III).

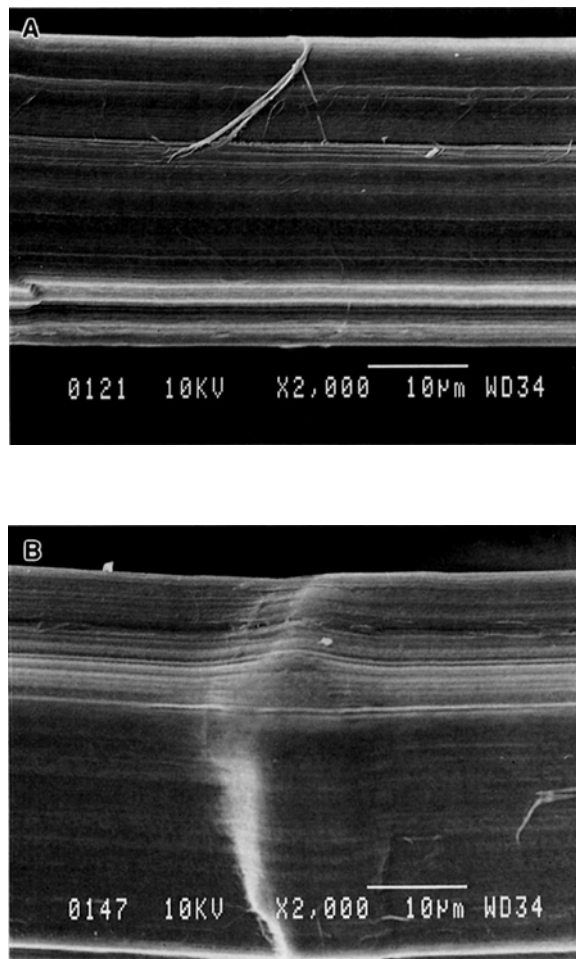
#### Hydrogen Peroxide Etching: Surface Texture and Surface Chemistry

A fibrillar texture similar to that previously described is revealed after 5 min etching with HP (Fig. 9). Increasing the etching time does not change this fibrillar structure substantially and there are no etching byproducts deposited on the fiber surface. There is 7% oxygen on the fiber surface after 5 min etching in Table I. This reduction in oxygen content reflects the removal of the oxidized surface layer without significant subsequent etching of the UHMWPE beneath. The spectra of the AR fiber and fibers after 4 h etching in different etchants can be compared in Figure 10. The HP-etched C1s spectrum in Figure 10(a) is relatively symmetrical, reflecting the dearth of carbon–oxygen bonds. The HP-etched O1s spectrum is relatively noisy, reflecting the reduction in the oxygen signal.

The FTIR spectrum in Figure 3 indicates a reduction in carbon–oxygen functional groups with HP etching. The ether peak ratio in Table II is significantly reduced, from 0.33 for the AR fibers to 0.06 for the fibers etched 4 h in HP. The carbonyl and carboxyl peaks are slightly reduced by HP etching. The removal of oxygen from the fiber surface as indicated in the ESCA results seems to be best reflected in the reduction in the ether peak ratios for all three etchants.



**Figure 8** ESCA spectra of PP etched fibers: (a) C1s; (b) O1s.

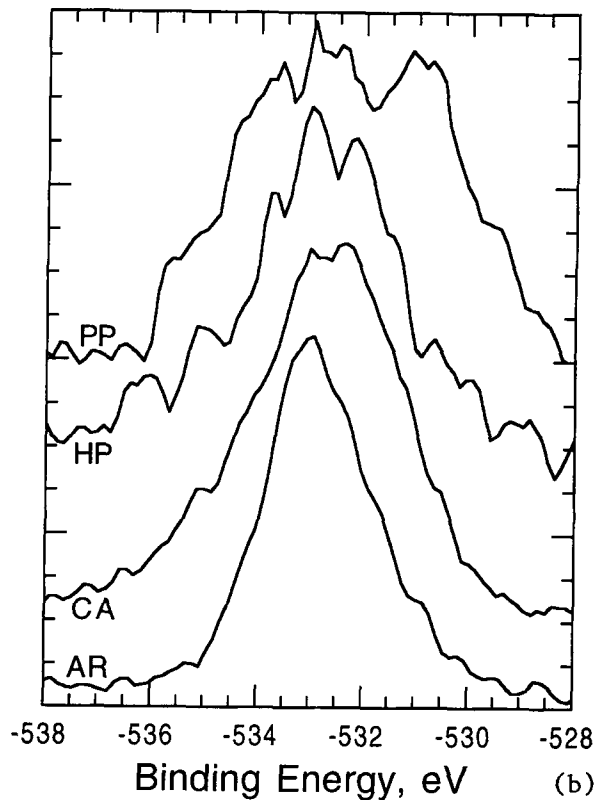
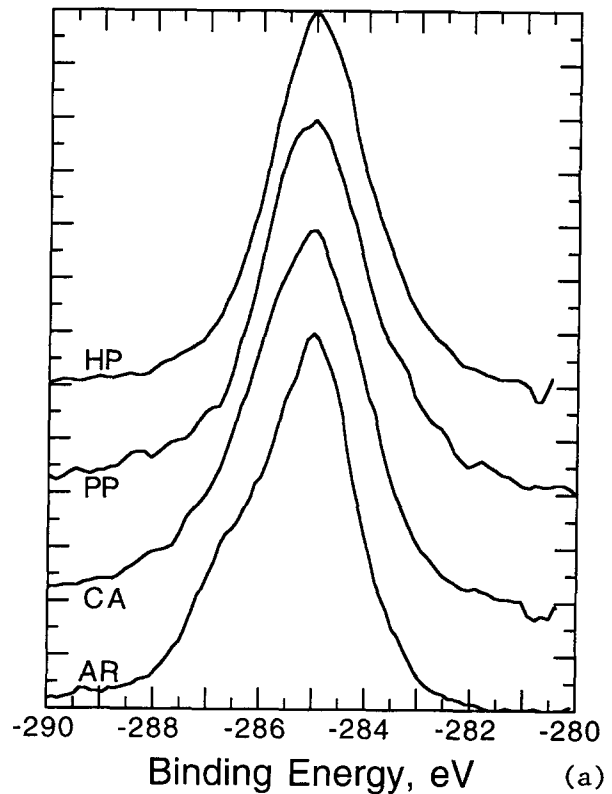


**Figure 9** SEM of HP etched fibers: (a) 5 min; (b) 4 h.

The HP seems to remove much of the oxygen-rich outer layer but does not etch the UHMWPE surface. The incomplete layer removal and reduction in oxygen helps explain the reduction in fiber-epoxy interfacial shear strength from that of the AR fiber (Table III). The interfacial shear strength for the HP-etched fiber was an order of magnitude less than that of the CA-etched fiber.<sup>4</sup>

## CONCLUSIONS

- The as-received fibers have a smooth surface with 22% hydroxyl and/or ether oxygen that could not be removed through washing with ethanol.
- This smooth surface reflects the presence of an outer layer, a weak boundary layer, which is largely removed by all etchants after 5 min etching. The oxygen on the fiber surface is re-



**Figure 10** ESCA spectra of fibers etched for 4 h with various etchants: (a) C1s; (b) O1s.

duced to less than 10% and the UHMWPE's oriented fibrillar hierarchical structure is exposed through etching. Further etching had little effect on the fiber.

- The UHMWPE fiber structure consists of an irregular cross section of approximately 25  $\mu\text{m}$  formed from bundles of oriented submicron fibrils that yield a corrugated surface texture. These microfibrils are interconnected by nanofibrils that are over an order of magnitude smaller.
- Chromic acid, the strongest etchant studied, yields a rough and oxidized UHMWPE surface. The oxidized UHMWPE includes ether and carbonyl bonds in a ratio of 6 : 1.
- The surface chemistry and topography characterization helps explain the significant improvement in adhesion with chromic acid etching in spite of the reduction in surface oxygen through the description of the removal of the outer layer, the increase in surface roughness, and the change in carbon-oxygen bonding.
- The surface of the hydrogen peroxide-etched fibers is relatively smooth and oxygen free, explaining the slight decrease in adhesion.
- The presence of manganese on the potassium permanganate-etched fibers indicates the formation of precipitates of manganese oxides and so the oxygen content of the fiber surface does not reflect UHMWPE oxidation.
- This research on chemical etching of UHMWPE fibers has explored the changes in surface chem-

istry and topography. The conclusions drawn from this characterization provide a sound basis for an understanding of the changes in other properties such as adhesion.

## REFERENCES

1. S. Borman, *Chem. Eng. News*, **67**, 23 (1989).
2. P. J. Barham and A. Keller, *J. Mater. Sci.*, **20**, 2281 (1985).
3. B. Tissington, G. Pollard, and I. M. Ward, *J. Mater. Sci.*, **26**, 82 (1991).
4. M. S. Silverstein and O. Breuer, *J. Mater. Sci.*, **28**, 4718 (1993).
5. A. J. Kinloch, *Adhesion and Adhesives*, Chapman & Hall, New York, 1987.
6. M. S. Silverstein and O. Breuer, *J. Mater. Sci.*, **28**, 4153 (1993).
7. M. S. Silverstein and O. Breuer, *Polymer*, **34**, 3421 (1993).
8. P. M. Sherwood, in *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, D. Briggs and M. P. Seah, Eds., Wiley, New York, 1983, p. 445.
9. J. Smook, W. Hamersa, and A. J. Pennings, *J. Mater. Sci.*, **19**, 1359 (1987).
10. Private communication.
11. A. J. Streitwieser, Jr. and C. H. Heathcock, *Introduction to Organic Chemistry*, Macmillan, New York, 1976, p. 289.

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