

Application of the Microbond Technique. IV. Improved Fiber–Matrix Adhesion by RF Plasma Treatment of Organic Fibers

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SYNOPSIS

The microbond technique is a modification of the single-fiber pullout test for measuring interfacial shear strength. Briefly, a cured microdroplet of material is debonded in shear from a single fiber. Ultra-high modulus polyethylene (Spectra) fibers and aramid fibers (Kevlar) were treated using a radio frequency plasma in order to increase the interfacial bond between the fibers and an epoxy resin. The treated fiber surface was subsequently analyzed by X-ray photoelectron spectroscopy (XPS). Plasma treatment resulted in an increased concentration of oxygen containing functionalities on the fiber surface. The interfacial shear strength as determined by the microbond test increased by 118% for the Spectra fibers and by 45% for the Kevlar fibers with the same epoxy resin. Scanning electron microscopy indicated little change of the surface topography of either fiber following plasma treatment. Effects of friction and surface composition of the plasma-treated fibers is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical properties and environmental stability of fiber-reinforced epoxy composites depends on the effectiveness of the interactions between fiber and matrix material.¹ This interfacial region of a composite transfers stress from the matrix to the fibers under load-bearing conditions. The mechanical properties of the interface are characterized chiefly by the interfacial shear strength, τ , between the fiber and its surrounding matrix. In order to enhance τ , one needs to modify either the matrix, the fiber, or both components. Fiber modifications are designed to alter the surface structure of the bonded material. This can be achieved by changing wettability, surface energy, surface roughness, and polar groups on the surface. All of these would improve adhesion. Chemical modification introduces polar groups or reactive sites that can form covalent

bonds, electrostatic, and/or van der Waals interactions between the matrix and the fiber. Physical modification of the fiber roughens the surface thereby increasing mechanical adhesion via interlocking between the fiber and its surrounding matrix. Mild oxidative treatments modify only the surface of the fiber either chemically or mechanically.

Plasma surface treatment is already used industrially to improve the painting performance of plastic automobile bumpers and the adhesion of epoxy resins to high-performance fibers. Aramid polymers such as DuPont's Kevlar® 49 and ultra-high modulus polyethylene (UHMPE) such as Allied Signal's Spectra® fibers are high-performance polymeric materials that have become increasingly important as strong lightweight reinforcements in organic matrix composites. The polyethylene fiber is chemically inert with no surface sites available for chemical or electrostatic bonding, while the surface of the aramid fiber is covered mainly with amide and carbonyl groups. Macroscopically both fibers are smooth-surfaced fibrillar structures with little rugosity to enhance mechanical interlocking. It has been reported by several authors that the interlaminar shear

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strength of composites made from these fibers increased by exposing the fibers to radio frequency (RF) glow discharge plasmas.²⁻⁷ Plasma modification is unique in that the surface structure of the polymer can be selectively modified while the bulk properties of the polymer remain virtually unchanged. Interfacial failure modes in these RF-treated fiber composites vary from adhesive failure to cohesive failure of the matrix and fiber splitting.

Currently, there are four micromechanical single-fiber test methods used to measure the interfacial shear strength in polymer-fiber composites. The first is the single-fiber fragmentation test⁸⁻¹¹ in which a single fiber is axially embedded in a dumbbell-shaped specimen of the polymer. The test coupon undergoes tensile loading with stresses transferred parallel to the fiber axis. The fiber tensile strength increases until the fracture strength is surpassed and the fiber breaks inside the matrix. A method that uses actual composite material is the microindentation or microdebonding test described by Mandell et al.¹² Sectioned composite laminates are the specimens used in this test whereby a load is applied to a probe that pushes out an individual fiber segment from the supporting matrix. Single-fiber pullout tests have been used extensively to investigate adhesion on model composite materials.¹³⁻¹⁶ In this technique a single fiber is embedded a short distance in or through a disk or button. The adhesion strength is then calculated from the force required to pull out the fiber divided by the embedded area of fiber in the matrix. In this simplest form the force required to extract the fiber varies with the embedded length in the matrix. Successful pullout experiments provide data on interfacial shear strength, the work of fracture, and frictional components after interphasial adhesion failure.

A modification of the single-fiber pullout test has been developed by Miller et al.¹⁷ This microbond technique involves depositing a small amount of resin on single fibers to form one or more discrete microdroplets on the surface. The cured microdroplets are then debonded in shear from the fiber. This method is a rapid and simple technique for determining interfacial shear strength in microcomposite samples.

In this study the relationship between fiber-matrix interactions and the interfacial shear strength of model microcomposites from an epoxy resin and organic fibers was investigated with the microbond technique for RF-plasma-treated fibers. Surface characterization was also used to examine the surface composition and morphology of the samples in this study.

EXPERIMENTAL

Materials

Commercial UHMPE fibers (Spectra® 1000 by Allied Signal, Petersburg, VA) were used as received in the microbond experiments. Aramid fibers (Kevlar® 49 by E. I. DuPont de Nemours, Wilmington, DE) are supplied with a "finish" and were successively washed in absolute ethanol or acetone to remove the finish. The fiber surface was inspected and the diameter was taken as the average of numerous fibers as determined by scanning electron microscopy (SEM). The commercial epoxy Epon® 828 (Shell Chemical Co., Montreal, Québec, Canada) and the aromatic amine curing agent, Tonox® (Uniroyal Chemicals, Elmira, Ontario, Canada) were mixed in 10 : 3 weight ratio in an aluminum pan at 60°C before deposition onto the fibers.

Small resin droplets were applied to the fiber using a fine-point applicator. As the applicator was withdrawn from the fiber, a small droplet formed around the fiber. The microcomposites were then cured under nitrogen atmosphere for 2 h at 90°C followed by 1 h at 120°C with subsequent cooling to room temperature at 2°C/min. Volatization of the curing agent from the droplet has been documented by Rao et al.¹⁸ Resin droplets were cured three ways; first as described above, then with a small amount of curing agent in a pan near the droplets to enhance the local concentration of curing agent vapors, and finally with resin samples in differential scanning calorimetry (DSC) pans. All exhibited similar properties under these mild curing conditions.

The embedded length of the resin droplets on the fibers was determined by optical microscopy prior to and following the microbond experiment. These ranged from 90 to 150 μm for the Kevlar samples and from 145 to 300 μm for the Spectra samples. The fiber specimens were glued on brass tabs with a commercial room temperature curing epoxy (Le-page Ltd., Boucherville, Québec, Canada).

Plasma Treatment

The plasma treatment was carried out in a Harrick plasma cleaner (model PDC-23G) at 50-60 W. Air was used as the "etching" gas. The Spectra and Kevlar fibers were plasma treated prior to deposition of the epoxy resin microdroplet. Several bundles of the fibers were placed on a glass support in the chamber. The chamber was evacuated to 60 mtorr before air was allowed into the chamber to an equi-

librium pressure of 500 mtorr for several minutes. Samples were plasma treated for periods ranging from 10 s to 5 min. Longer treatment times proved deleterious as evidenced by fiber melting and kinking. Following the treatment, the chamber was flooded with air until atmospheric pressure was attained. Fiber samples were then mounted as described above.

Surface Characterization and Morphology

The surface of carbon fibers and epoxy resin were examined by X-ray photoelectron spectroscopy (XPS), which provides information on the surface composition of the fiber before and after plasma treatment. Spectra were collected on a PHI-5500 spectrometer equipped with an X-ray monochromator using an aluminum anode (1486.6 eV). The pressure in the sample chamber was lower than 10^{-9} torr. High-resolution data were obtained with 29 eV pass energy, while survey spectra were acquired with 187 eV pass energy. The X-ray spot size was 1 mm \times 3 mm. All spectra were referenced to the C1s peak for neutral carbon, which was assigned a value of

284.6 eV. Scanning electron micrographs (SEMs) were taken on a Joel JSM-84 electron microscope.

Apparatus

The microbond technique has been previously described by other workers.^{16,17,19} Essentially, a microdroplet of polymeric resin is deposited on the surface of a fiber, which is fastened to a brass tab hung on the crosshead of an Instron (model 1123). The upper surface of the droplet is gripped by two flush stainless steel blades secured to a microvise as schematically shown in Figure 1. The droplet was debonded in shear by an upward displacement of the crosshead at a speed of 0.5 mm/min. The output of the Instron was interfaced to an Epson personal computer in order to display, store, and analyze the data. The shearing force at the interface is transferred to the fiber-resin interface and is recorded by the load cell. The pullout force is recorded as debonding proceeds, and the interfacial shear strength is calculated using

$$\tau = \frac{F}{\pi dl} \quad (1)$$

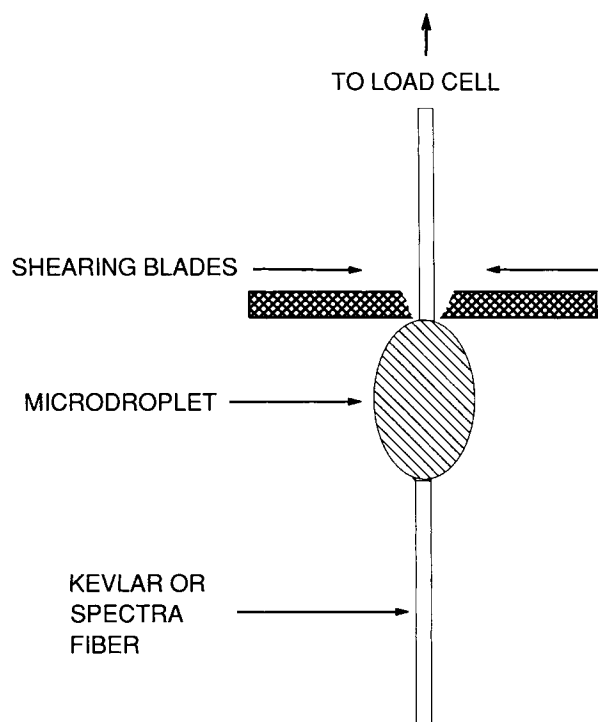


Figure 1 Schematic diagram of the microbond test. The polymer fiber was suspended from the crosshead from a brass tab while the resin droplet was sheared away in tension by two blades attached to a microvise. The microvise remained fixed while the crosshead translated upwards.

where F is the pullout force, d is the diameter of the fiber, l is the embedded length of the resin droplet. Drop size distributions were similar for all experiments. Resin cure and glass transition temperature were determined by DSC on a DuPont 910 coupled to a DuPont 1090 thermal analysis system. The glass transition temperature of the cured resin was 118°C.

RESULTS AND DISCUSSION

Microbond

The interfacial shear strength (IFSS) of microcomposites of plasma-treated Spectra and Kevlar fibers and epoxy resin was determined by the microbond technique. A typical trace for a microbond experiment is shown in Figure 2. The sampling rate was 10 Hz. Faster sampling rates (i.e., 100–200 Hz) did not reveal additional insight to the debonding process in the recorded traces. The IFSS of untreated samples was lower than treated samples indicating improvement of fiber-matrix interactions (Table I). The IFSS of the microcomposites in the present study increased with exposure time to the air plasma for the spectra fiber composites. A 10-s treatment

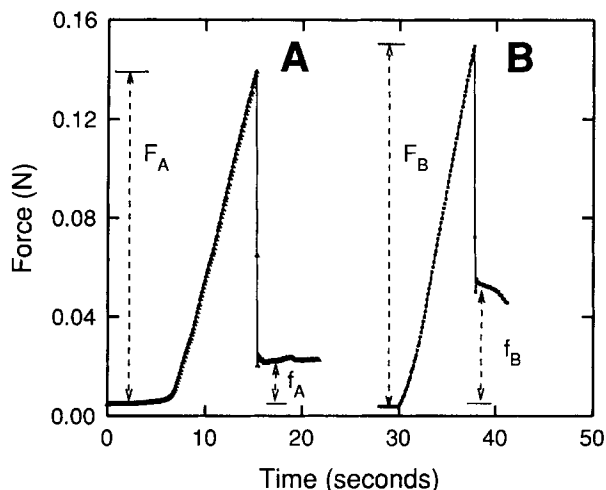


Figure 2 Typical force versus time trace for a microbond experiment for the system Kevlar 49 and Epon 828 epoxy resin. The sampling rate was 10 Hz.

increased the shear strength by 38%, while a 2-min plasma exposure time more than doubles the IFSS from 8.6 to 17.4 MPa. The effect of treatment time on the IFSS is shown in Figure 3. There was a 66% increase in shear strength within the first 30 s of RF plasma treatment. Longer plasma irradiation periods such as 5 min improved the shear strength by 118%. This is the first report of IFSS of Spectra 1000 with Epon 828 resin using the microbond technique. Chappell et al.⁵ reported a value of 5.7 MPa

Table I Interfacial Shear Strength of Spectra® 1000 UHMPE Fibers with Epon® 828 and Kevlar® 49 Aramid Fibers with Epon® 828 Epoxy Resin as Determined by Microbond Technique

Fiber Treatment	Spectra 1000	Kevlar 49
	Interfacial Shear Strength (MPa) ^{a,b}	
None	8.6 ± 1.3 (30)	32.8 ± 3.9 (35)
10 s in air plasma	11.9 ± 1.9 (37)	42.4 ± 5.4 (43)
30 s in air plasma	14.3 ± 1.7 (32)	45.9 ± 2.4 (31)
100 s in air plasma	14.8 ± 0.9 (30)	46.5 ± 4.5 (39)
120 s in air plasma	17.4 ± 1.0 (30)	—
180 s in air plasma	17.2 ± 1.5 (34)	—
200 s in air plasma	—	47.7 ± 4.6 (33)
300 s in air plasma	18.7 ± 2.3 (33)	43.7 ± 3.1 (32)

^a Variations expressed as standard deviations from the mean.
^b Numbers in parentheses represent number of successful debonds.

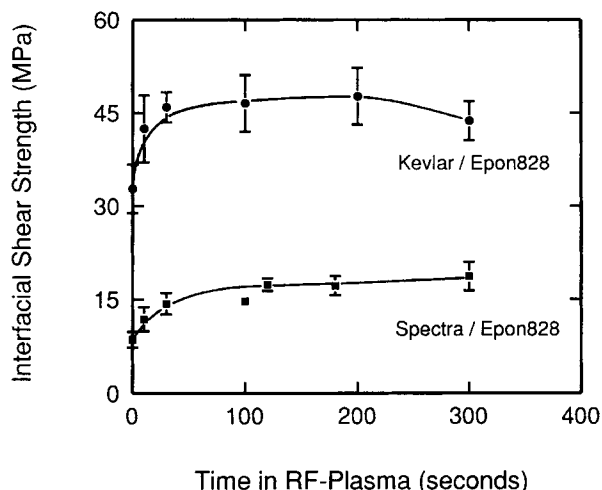


Figure 3 Plot of interfacial shear strength of Spectra-Epon 828 microcomposites (■) and Kevlar-Epon 828 (●) as a function of treatment time in the RF plasma. Error bars represent standard deviation from the mean value as determined from the microbond test.

for interlaminar shear strength of untreated composites and 6.6 MPa for oxygen-plasma-treated samples. Ammonia-plasma-treated samples displayed 11.8 MPa of interlaminar shear strength. It should be noted that the test procedures and the epoxy curing agent differ in the present case and only qualitative comparisons can be made with Chappell's work. Fiber bundle pullouts for Spectra 1000 and a polyester resin was studied by George and Willis.²⁰ Single-fiber pullouts on melt-spun UHMPE at several draw ratios exhibited an increase in IFSS with oxygen plasma treatment from 0.5 to 2.7 MPa.⁶ The difference in shear strength values obtained in this report and those of Chappell et al.⁵ is attributed to the different test methods. In the latter, the short-beam shear test was used while this work focuses on a single-fiber testing technique.

Once the specimen was debonded, it began to slide along the fiber with accompanying friction. Control samples slid along the fiber with an average frictional force of 0.01 N or about 10.2% of τ . This was in contrast to 2-min plasma-treated samples in which frictional components amounted to 14% of τ while the samples treated for 5 min displayed frictional components amounting to 25% of the IFSS. The increase in friction with plasma irradiation time follows a similar, but less pronounced trend as the increase in τ . Surface chemical changes on the UHMPE fibers are the most likely cause for these increases although mechanical adhesion attributed to surface rugosity at the submicron level cannot be

overlooked. Both these factors will be discussed later.

Kevlar 49 fiber-epoxy composites exhibited an increase in IFSS with plasma treatment time (Table I). The 30-s plasma treatment yielded a 40% increase in τ over the control microcomposites. The 200-s treatment produced the best increase for the aramid fiber, 47.7 MPa. This corresponds to a 45% improvement. A longer plasma treatment of 300 s weakens the interfacial strength to 43.7 MPa suggesting that a layer of loosely bound "skin" material had been weakened by the extended treatment time. This is still an improvement over untreated Kevlar fibers, but not as high as the 200-s plasma treatment. The temporal behavior of the IFSS with plasma irradiation of the fiber is shown in Figure 3.

Other workers have studied the Kevlar-Epon 828 system^{7,16,17} using the microbond technique but with different curing agents and cure schedules than the present work. Gaur and Miller²¹ have determined τ to be 41.4 MPa. In separate work on hydrothermal effects of Kevlar composites, a value of 31.7 MPa was reported.²² This is similar to 32.8 MPa for the control Kevlar samples in this study. Küpper and Schwartz⁷ obtained 26.7 MPa for Kevlar 49-DER 331 epoxy with an aliphatic amine curing agent. These workers plasma treated the fibers in Ar, CO₂, and N₂ with interfacial shear strength improvements ranging from 11 to 18% over the control samples. This is lower than the plasma improvements reported here primarily since air is a more oxidizing "etching" gas. The radicals formed during the plasma treatment may react further with atmospheric oxygen following the treatment.

Following debonding, the frictional force was 33% of the IFSS for the Kevlar control samples. After plasma treatment of the fiber, the frictional component following debonding was between 16 and 21% of the IFSS. This is in contrast to the increase in friction with the UHMPE plasma-treated samples described above where the frictional component increased with plasma treatment time. The chemical surface changes by oxidation and surface crosslinking are similar in both cases yet the results of adhesion strength are different. The concentration of carbonyl, hydroxyl, carboxylic acid, and amide surface groups on both fibers, their wettability, and mechanical pressure attributed to shrinkage differences between fiber and epoxy during the curing process will affect this friction component as well as the value of the IFSS. These differences in adhesion and friction following debonding may be accounted for by the different surface energies of the control and treated samples.

Microscopy

The plasma treatments did not affect the diameter of the fibers as seen by electron microscopy. The tensile strength of the fibers did not change significantly ($\pm 5\%$) following the plasma treatments. Optical and scanning electron micrographs were obtained for both the UHMPE and aramid microcomposites before and after plasma treatments and microbonding experiments. There appears to be little difference in either fiber surface before and after plasma treatment (Figs. 4 and 5). If there is any micropitting, which can contribute to mechanical interlocking between the epoxy and the fiber, it must be on the submicron level. The morphology of the surface before and after microbonding was examined by SEM. Higher magnification of fibers indicates a similar surface as shown in the micrographs. There was no relationship between the surface morphology and the IFSS of the plasma treatment Spectra or Kevlar-epoxy microcomposites. This is similar to the results of other workers,^{7,19} but in contrast to the micrographs of Ladizesky and Ward,⁶ which clearly shows a cellular structure of the plasma-treated drawn polyethylene monofilament. However, both the fibers and plasma treatment in this case are different from those of Ladizesky and Ward mentioned above, therefore only qualitative comparisons can be made. Mechanical keying and interlocking may play a role in adhesion for UHMPE and aramid fibers with epoxy, but our SEM results cannot confirm a significant change in the surface morphology. In metal oxides, pore sizes of less than 20 nm have been shown to promote mechanical interlocking. There was no evidence of such morphological features with these polymeric fibers in this case.

We also observed that there was no resin remaining on the debonded length of fiber following pullout. This seems to point toward an adhesive mode of failure at the interfacial area closest to the fiber. A cohesive failure of the resin droplet would have left bits of resins attached to this debonded length. This could have significantly increased the frictional force. There was no fibrillar cohesive failure of the UHMPE or aramid fibers as reported by other workers.^{5,7,23} The fibrils, which peeled off in the cases of Chappell et al.⁵ and in the cases of Haaksma and Cehelnik,²² may be related to surface defects on the fibers. There may be a weak outer layer on the UHMPE and aramid fibers (perhaps on the nanometer scale), which participates in interfacial bonding and is peeled away with the resin leaving a bare fiber following debonding. The fi-

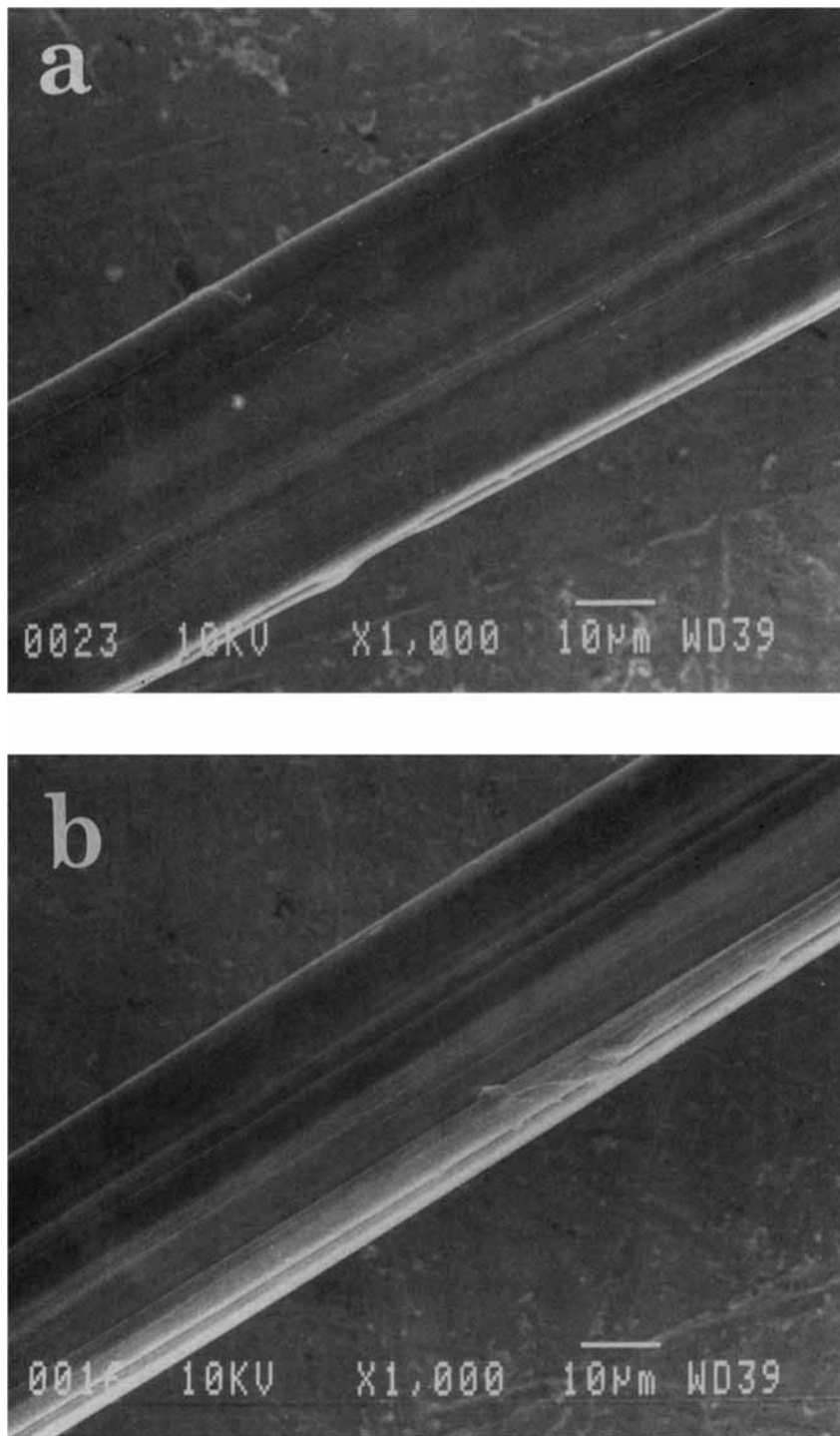


Figure 4 Scanning electron micrographs of Spectra 1000 UHMPE fibers (a) before and (b) after plasma treatment for 180 s. Micrographs of Kevlar 49 fibers (c) before and (d) after plasma treatment for 200 s.

brillar character of both fibers results in a breakdown within the “skin” of the fiber regardless of the type of chemical or plasma treatment given to the fibers.²⁴

The values of adhesion produced here approach the values reported for all methods and represent a plateau that cannot be surpassed because of the fiber

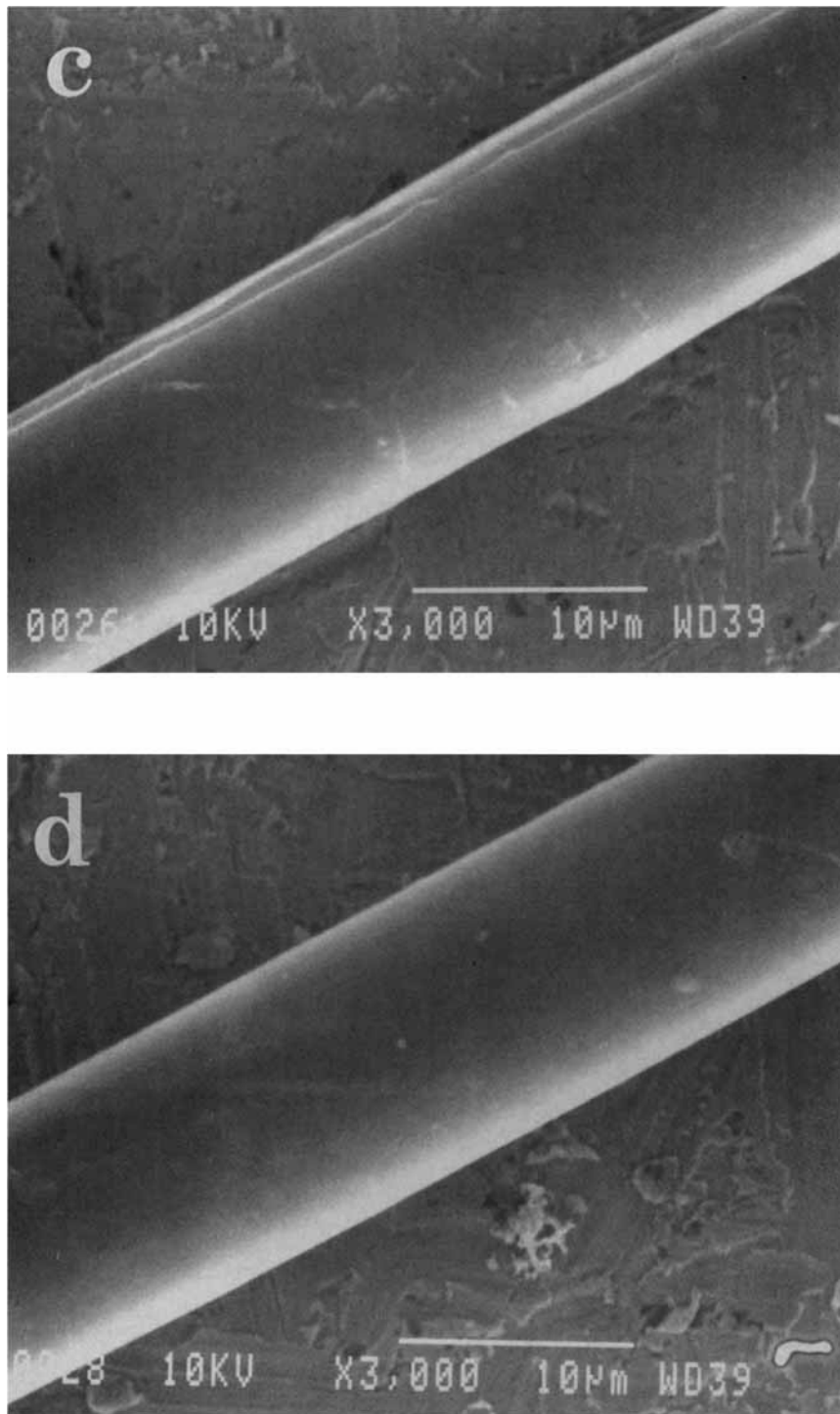


Figure 4 (continued from the previous page)

microstructure. The improvement in adhesion is primarily due to the removal of low molecular weight material from the fiber surface.

Improving adhesion between fibers and matrices is the primary aim of plasma treatments. The par-

ticular plasma chemistry depends on the type of gas used in the treatment. Argon plasma introduce active sites (radicals), which react with atmospheric oxygen following the treatment. Oxygen plasma also introduces active sites as well as oxygen atoms di-

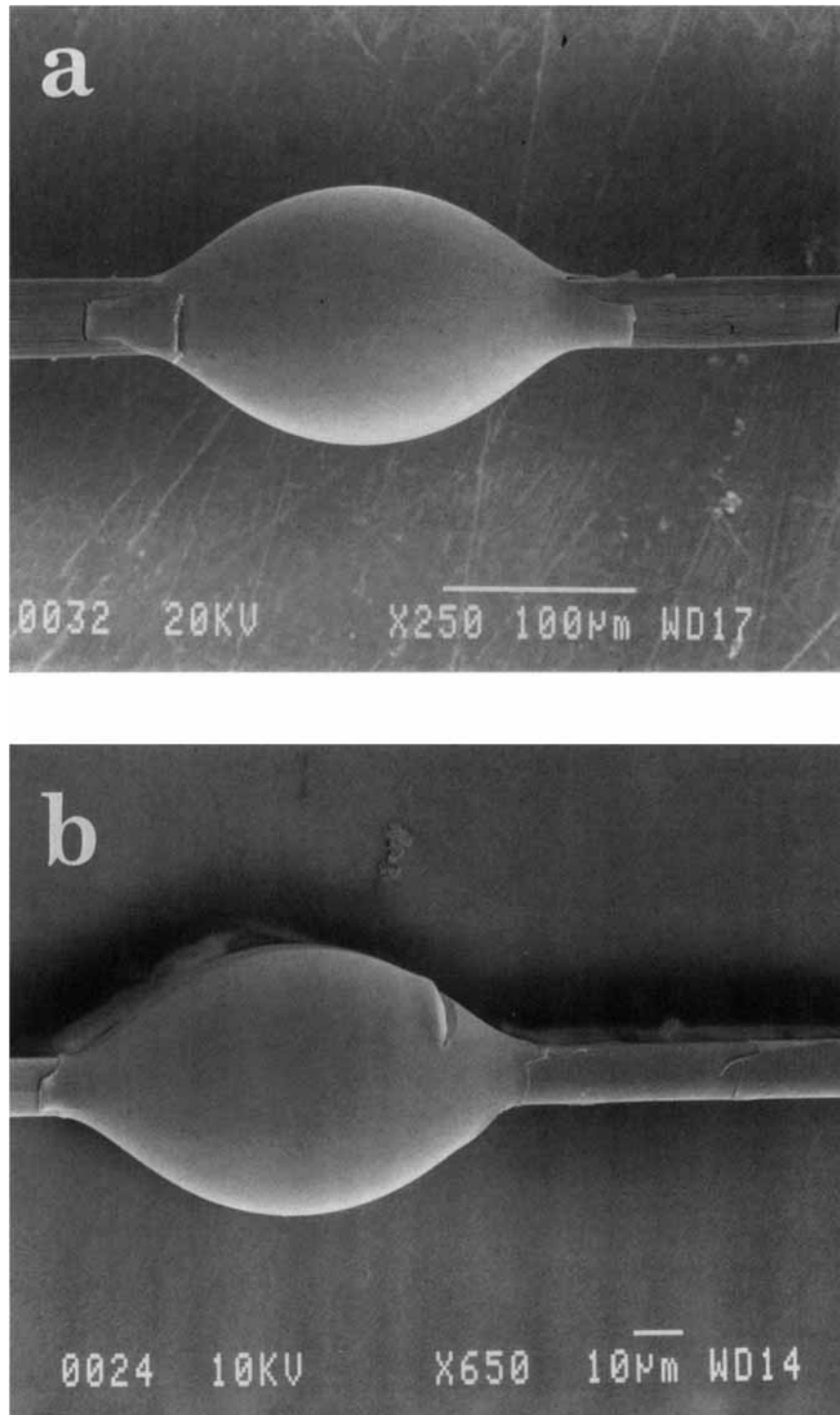


Figure 5 Scanning electron micrographs of Spectra-Epon 828 microcomposites (a) after the microbonding experiment. A Kevlar-Epon 828 microcomposite (b) after the microbond experiment is also shown.

rectly to the surface and by the above mechanism. Inert gases in plasma treatments generally form radicals and subsequent surface crosslinking, while

oxidizing gases produce oxidation, etching, and degradation. Air plasmas produce surfaces with characteristics of both inert and oxidizing plasmas.

Table II Atomic Surface Concentration by XPS of Spectra 1000 Fibers Following RF Plasma Treatment

Treatment Time in RF Plasma (air @ 0.5 torr)	Surface Concentration of Carbon (%) ^a	Surface Concentration of Oxygen (%) ^a	O1s C1s
Control	98.3 ± 0.7	1.4 ± 0.5	0.014
10 s	80.7 ± 2.2	17.1 ± 2.4	0.222
30 s	82.3 ± 0.1	17.0 ± 0.1	0.207
60 s	82.8 ± 0.6	16.4 ± 0.6	0.198
120 s	83.7 ± 1.3	15.5 ± 1.3	0.186
300 s	79.1 ± 2.5	20.9 ± 2.5	0.264

^a Variations are expressed as standard deviations from mean values.

It is also probable that other factors such as radial compressive stresses, van der Waals forces, hydrogen, and/or covalent bonding may be contributing to the observed increase in IFSS between Spectra fibers and the epoxy resin with plasma treatment.

X-ray Photoelectron Spectroscopy (XPS)

Chemical bonding information can be obtained with XPS. It has been used to study the functional groups on the surface of a variety of fibers. Unfortunately, the interfacial region is not directly accessible with XPS, and only the surface prior to the formation of the interface can be studied.

Control samples of Spectra fibers display a large carbon peak and a small oxygen peak (1% atomic concentration) while plasma-treated samples show an abundance of oxygen containing surface species as shown in Table II. The amount of surface oxidation is evident in the O1s/C1s ratios. In the XPS survey spectra of control and plasma-treated fibers, only the characteristic C1s and O1s photopeaks were observed and became asymmetric as surface oxidation progressed by plasma treatment. There was no significant quantity of nitrogen containing surface species even though the etching gas was air ($\approx 79\% \text{ N}_2$). Surface oxygen concentrations rose rapidly and accounted for 20% of the atomic concentration on the surface of the fiber between 10 s and 2 min of plasma irradiation. After 5 min, the O1s/C1s ratio is 0.264. This ratio is greater than the O1s/C1s ratio for hydroperoxidation but closer to the values obtained for corona discharge treatment.¹⁹ This plasma treatment resulted in high values of τ and could be related to surface groups that originate from C—O-type functionalities. High-resolution XPS of the C1s region show that carbon-based oxygen functionalities are present as indicated by the

different shape of the carbon peak (Fig. 6). Spectral deconvolution of the C1s bands of plasma-treated samples indicates that hydroxyl, ether, aldehyde, ketone, carboxylic acid, and carbonate groups are present on the surface. The relative concentration of these groups as a function of plasma irradiation is presented in Table III. The increased amount of the groups may provide additional sites for chemical bonding. The reaction of these groups with epoxy is well documented.²⁵ Furthermore, the amine curing agent can react with these groups.

Attenuated total reflectance (ATR) FTIR was used in parallel to qualitatively compare the types of functional groups on the surface of plasma-modified polyethylene. HDPE sheets, which closely re-

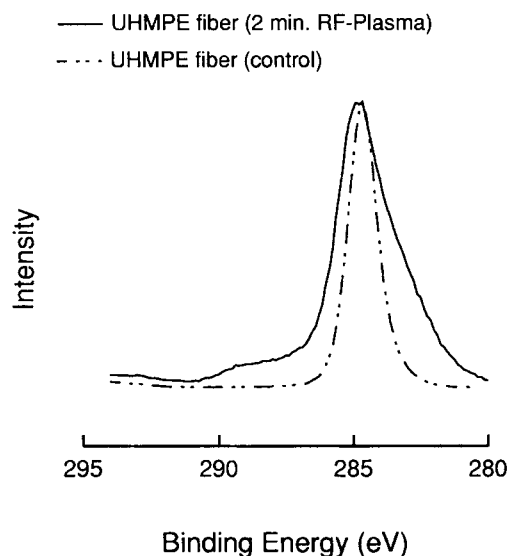


Figure 6 X-ray photoelectron spectra of the C1s region of control UHMPE fibers and 2-min plasma-treated UHMPE fibers.

Table III Percentage of Total C1s Peak Area of Spectra 1000 Fibers Following RF Plasma Treatment

Treatment Time in Plasma (air @ 0.5 torr)	% Carbon Functionality			
	$\begin{array}{c} \text{---}\underline{\text{C}}\text{---OH} \\ \text{---}\underline{\text{C}}\text{---O---C} \end{array}$	$\begin{array}{c} \text{---}\underline{\text{C}}\text{=O} \\ \text{---}\underline{\text{C}}\text{=O} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{---}\underline{\text{C}}\text{=O} \\ \\ \text{OH} \\ \text{---}\underline{\text{C}}\text{=O} \\ \\ \text{OR} \end{array}$	$\text{---}\underline{\text{C}}\text{O}_3$ Type
Untreated	1.4	—	—	—
1 min	5.6	2.0	3.3	1.3
5 min	7.4	4.3	3.2	1.4

sembles Spectra, were plasma treated in the same manner as described in the experimental section and mounted on KRS-5 crystals. ATR-FTIR spectra are shown in Figure 7. The plasma treatment resulted in an increase in absorbance of species at 1600, 1640, 1720 (ketones), and 1750 cm^{-1} (C=O of esters). These latter increases in absorbances parallel the XPS results for plasma-treated samples of Spectra, which show an increase in the ketonic and ester species following treatment (Table III).

On any modified surface, including UHMPE fibers, demonstrating direct evidence of chemical bond formation is difficult at best. Hydrogen bonding and secondary bonding (van der Waals forces) probably play important roles in chemical aspect of bonding in composites of this type. The physical bonding as a result of mechanical keying between epoxy and fiber can occur in highly oxidized fiber surfaces where resin can be trapped in pores or pits along the fiber surface. This type of change in surface morphology may not be as evident in this case because air, not oxygen, was used as the etching gas. If surface etching has occurred, it was on the sub-micron level.

The effect of air plasma treatment on UHMPE fibers increased the surface oxidation of the fibers. Microcomposites of Spectra 1000 with Epon 828 show significant improvement fiber-matrix adhesion as indicated by microbond experiments. These results coupled with XPS and SEM suggest that mechanical interlocking of resin and fiber may be less important than chemical bonding (electrostatic or covalent), hydrogen bonding, and van der Waals interactions. Furthermore, the introduction of surface oxygen functionalities increases the surface polarity leading to better fiber wet-out. Similar interactions with the resin may also improve interfacial mechanical properties. Residual radical species left

over after the plasma treatment may facilitate interfacial bonding as well.

The Kevlar 49 fibers were studied by XPS before and following plasma treatment. Atomic concentrations of carbon, oxygen, nitrogen and sodium on the surface of the aramid fibers is presented in Table IV. These values reflect surface amine, amide, carbonyl, hydroxyl, phenyl, and carboxylic functionalities as indicated by shifts in corrected binding energy positions in the high-resolution photoelectron spectra. An electron flood gun was used to neutralize charging of the Kevlar fibers. From the composition values of Table IV, the fiber's surface chemistry after 30 s of plasma treatment begins to resemble that of Kevlar 49 reported by Morgan and Allred.²⁶ There were traces of sodium and sulfur (probably present as Na_2SO_4), which are impurities remnant of H_2SO_4 and NaOH used in the production of the fiber. The plasma treatment presumably ablated a layer a few nanometers thick away from the aramid fiber leaving a surface with a higher surface energy.

The O1s/C1s ratios decreased as the N1s/C1s ratios increased with plasma treatment. It can be speculated that this is the result of the production of more amine-type species on the surface. These species are capable of reacting with the epoxy thus forming stronger interfacial interactions. The observations that an increase in % N from 0 to 100 s plasma treatment was 47% and the increase in interfacial shear strength for the same period was 42% seem to support this hypothesis. The relative augmentations are similar, and other interactions such as van der Waals and electrostatic interactions probably play a role in Kevlar-epoxy adhesion. The increase in surface nitrogen is analogous to experiments where ammonia plasmas were used. In these experiments, interlaminar shear strengths were in-

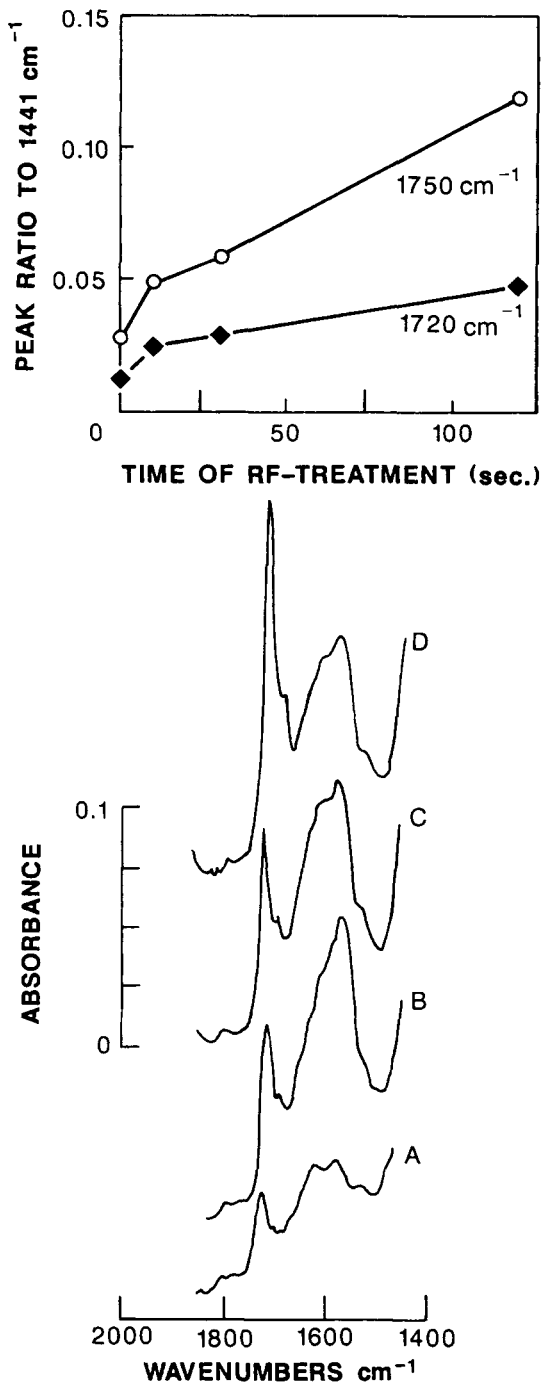


Figure 7 (a) Attenuated total reflectance FTIR spectra of control, and plasma-modified HDPE for (b) 10 ss, (c) 30 ss, (d) 2 mins. Inset shows absorbance at 1720 cm⁻¹ and 1750 cm⁻¹ normalized to 1441 cm⁻¹ (C—C polyethylene) as a function of plasma treatment time.

creased in aramid-epoxy composites.²⁷ There was no increase in nitrogen-containing species for Spectra fibers treated in air plasma suggesting that the

surface energies for nitrogen species is low on the polyethylene fibers.

The surface energy of Kevlar 49, γ , is composed of a dispersive component, $\gamma^d = 38.0 \text{ mJ/m}^2$, which overshadows the acid-base forces, $\gamma^{a/b} = 10.5 \text{ mJ/m}^2$.²⁸ There is a favorable matching of surface energies between the aramid fiber and the bisphenol-A epoxy used in this experiment since the latter epoxy has $\gamma^d = 35.5 \text{ mJ/m}^2$ and $\gamma^{a/b} = 12.0 \text{ mJ/m}^2$. Polyethylene's surface energies are $\gamma^d = 31.3 \text{ mJ/m}^2$ and $\gamma^{a/b} = 1.1 \text{ mJ/m}^2$,²⁹ which do not match as well as the aramid fiber-epoxy interactions. This is the simplest thermodynamic reason why the lower energy surface of Spectra fibers does not form as strong an interfacial shear bond with the epoxy as does the aramid fiber in the untreated state. Following plasma treatment, the polar and dispersive components of the surface free energy are more likely to rise, creating a better matching of surface energies between the fiber and epoxy. In turn, the epoxy wets out better on the plasma-treated fiber.

CONCLUSION

The effect of air plasma treatment on UHMPE fibers increased the surface oxidation of the fibers. Microbond experiments on microcomposites of Spectra with Epon 828 show significant improvement in fiber-matrix adhesion. These results coupled with XPS and SEM analysis suggest that mechanical interlocking of resin and fiber may be contributing less than chemical bonding (electrostatic or covalent), H-bonding, and van der Waals interactions. Furthermore, the introduction of surface oxygen functionalities increases the surface polarity leading to better fiber wetout. Similar interactions with the resin may also improve interfacial mechanical properties. Residual radical species left over after the plasma treatment may facilitate interfacial bonding as well. The effect of air plasma treatment on Kevlar fibers is to increase the interfacial shear strength of aramid-epoxy model composites. Surface changes are different in the aramid fiber case, and it appears that secondary forces are more important than mechanical interlocking as in the polyethylene fiber case. Both systems fail adhesively at the interface with no residual resin remaining on the fiber. It has been shown that the microbond technique can be used to study the interfacial shear strength and frictional components of model composite systems that have been surface modified by plasma treatment.

Table IV Atomic Surface Concentration by XPS of Kevlar 49 Fibers Following RF Plasma Treatment

RF Treatment Time (s) (air @ 0.5 torr)	%C ^a (C1s)	%O ^a (O1s)	%N ^a (N1s)	%Na ^a (Na2s)	O1s/ C1s	N1s/ C1s	Na2s/ C1s	τ (MPa)
Control	71.6 ± 0.4	23.1 ± 0.4	4.8 ± 0.2	5.0 ± 0.3	0.323	0.067	0.007	32.8
10	70.1 ± 0.9	23.0 ± 0.6	5.8 ± 0.8	1.1 ± 0.3	0.328	0.083	0.015	42.4
30	68.6 ± 2.4	23.3 ± 2.1	7.4 ± 0.3	0.7 ± 0.1	0.340	0.108	0.010	45.9
100	69.3 ± 0.8	22.8 ± 0.6	7.0 ± 0.5	0.9 ± 0.6	0.330	0.101	0.011	46.5
200	69.5 ± 0.5	21.4 ± 0.5	7.5 ± 0.5	1.6 ± 0.5	0.307	0.108	0.022	47.7
Allred & Morgan ²⁴	68	25	7	—	0.367	0.103	—	—

^a Variations are expressed as standard deviations from mean values.

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