Surface Modification of UHSPE Fibers through Allylamine Plasma Deposition. II. Effect on Fiber and Fiber/Epoxy Interface

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SYNOPSIS

The surface of ultra-high strength polyethylene (UHSPE) fibers was modified using allylamine plasma deposition to improve their adhesion to epoxy resins. Allylamine plasma polymerization was investigated at different power inputs and polymerization times. The adhesion of treated fibers to epoxy resin was studied by single-fiber, pull-out tests. A special silicon rubber mold was developed to embed the single fiber in epoxy resin. The results show that the interfacial shear strength (IFSS) increased by a factor of 2 to 3 after allylamine plasma treatments. The greatest improvement, by a factor of 3.25, was obtained at 30 W for 10 min. Scanning electron microscopy (SEM) was also used to study the surface topography of fibers pulled from the epoxy resin. In most cases, it was observed that pull-out failure occurred at the interface, as evidenced from clean fiber surfaces. In a few cases, however, fibrils were peeled from fibers. The fiber strength decreased, but initial modulus increased after the plasma treatments. The decrease in fiber strength was insignificant for treatments at a lower power input, but was significant at higher power inputs. Treatment time, however, had no significant effect on fiber strength.

INTRODUCTION

High-strength, light-weight structural composites made from fibers, such as aramid, graphite, and ultra-high strength polyethylene (UHSPE), are beginning to be used routinely in place of more conventional metals and metallic alloys. In these cases weight savings are an important consideration. Among most high performance fibers, UHSPE fibers show high strength, comparable with others, but have the lowest density, as shown in Table I. UHSPE fibers are spun from ultra high molecular weight polyethylene (UHMWPE), ($M_n = 2 \times 10^5$ vs. $M_n = 5 \times 10^3 - 4 \times 10^4$ for conventional polyethylene fibers) by gel spinning process.[1-4] The high draw ratio in gel spinning causes the molecules to fully extend, developing close to 100% orientation in crystalline regions.[5] As a result, they have the highest specific strength and modulus. They also

exhibit higher impact toughness, abrasion resistance, and chemical resistance than aramid fibers.[1] The UHSPE fibers, as a result, are now replacing aramid fibers for such uses as antiballistic applications, marine ropes, sails, surgical gloves, etc. UHSPE fibers also have the lowest dielectric constant and loss tangent, and the highest transmission coefficient to radar wave, among the reinforcing fibers. Consequently, UHSPE fiber composites especially made from polyethylene resins are excellent materials for radome.[6,7] UHSPE fiber composites have unusually higher impact and flexural toughness than carbon and glass fiber composites.[8,9] Their impact energy absorption can be up to six times that of aramid fiber composites.[8] The combination of impact and flexural toughness of UHSPE fibers with high stiffness of carbon fibers or high strength of glass fibers to tailor the properties of hybrid composites, can be used to meet any requirements for most low temperature applications.

UHSPE fibers, however, have the poorest adhesion to matrices, the lowest melting point, and the highest creep among all the reinforcing fibers. These

Table I   Properties of Reinforcing Fibers[1-3]

Property		UHSPE Spectra 900	UHSPE Spectra 1000	Aramid Kevlar 49	S Glass	Graphite HM
Density	(g/cm³)	0.97	0.97	1.44	2.55	1.81
Strength	(MPa)	2586	2999	2758	4585	2413
Specific strength	(10³ m)	272	315	198	188	137
Modulus	(GPa)	117	172	124	90	379
Specific Modulus	(10⁶ m)	12.3	18.1	8.8	3.6	21.6
Elongation at break	(%)	3.5	2.7	2.8	5.7	0.6
Abrasion resistance	(cycles to break)	> 110 × 10³		5.7 × 10³	—	120
Flex life	(cycles)	> 240 × 10³		43 × 10³	—	2
Max. working temp.	(°C)	130		180	250	> 1500

undesirable properties limit the fibers' use in advanced composites. The fundamental cause of poor adhesion of UHSPE fibers to matrices lies in their chemical composition, consisting solely of methylene groups. The nonpolar nature makes them difficult to wet and impossible to be chemically bonded to matrices. Besides, UHSPE fibers also have smooth surfaces, which exclude mechanical interlocking, and their relatively larger diameters reduce the specific contact area with matrices. Comparative interlaminar shear strength values of major fibers used in composites are given in Table II.[2,10]

Since UHSPE fibers have been developed only recently, very few methods have been developed to improve their bondability to matrices. UHSPE fibers are inert and most of the surface modification methods available to the other reinforcing fibers and conventional polyethylene fibers and films cannot be employed to modify UHSPE fiber surface. Oxidation in chromic acid[11] and sulfonation in chlorosulfonic acid[12] have been reported in the literature. These methods require a prolonged immersion of the fibers in acids in order to have a significant improvement in interfacial bond strength, and they are accompanied by an undesirable loss in fiber strength. Oxidation of UHSPE surface was also tried through corona discharge and flame treatment,[2] often re-

sulting in considerable increase in interlaminar shear stress without significant loss in fiber strength. However, such treatments could be inherently hazardous to the fibers because the process conditions are difficult to control.

Plasma treatment may be a better way to modify the surface for improving adhesion. When a gas is electromagnetically excited or electrically charged at a low pressure, typically 0.1–10 torrs, a glow discharge similar to corona discharge in air, referred to as plasma, is produced. Plasma contains free radicals, an equal number of positive ions and electrons, and natural species. The activated species can readily react with any solid organic materials in contact. Plasma treatment may be divided into polymerforming and non-polymerforming plasmas. Plasmas of gases, such as oxygen, nitrogen, hydrogen, ammonia, and argon, are non-polymerforming. They modify fiber surface chemistry by reacting with fibers through abstraction of hydrogens in polymer chains and by creating free radicals that later are oxidized into hydroxyl and carbonyl groups when exposed to air. Polymerforming plasmas are formed by most organic gases or vapors from many liquids or mixtures of some non-polymerforming gases. They yield polymeric film deposition, often with reactive functional groups, onto fiber surface or any other substrates. Ladizesky and Ward[11] found that oxygen plasma treatment increased interfacial bond strength significantly but at the expense of fiber strength. Most recently, Holmes and Schwartz[13] treated UHSPE fabrics with ammonia plasma. Their results indicated improved adhesion of the fabrics to epoxy resin without affecting the fiber strength. Kaplan et al.[2] and Ngyuen et al.[14] treated Spectra fibers with some unspecified, non-polymerforming

Table II   Interlaminar Shear Strength (ILSS) of UHSPE Fiber Composites and Other Reinforcing Fiber Composites[2,10]

Fiber	UHSPE	Aramid	Carbon	Glass
ILSS (MPa)	8–17	21–40	66–110	55–97

gas plasmas. Their results showed a twofold increase in interlaminar shear strength (ILSS) without much loss in fiber strength.

Although non-polymerforming plasma treatments are popular for surface modification of fibers and polymerforming plasma, treatments have also been widely used for a wide range of applications.[15,16] However, fiber surface modification through polymerforming plasma treatment has been very limited. Sung et al.[17] treated carbon fibers with acrylonitrile plasma and found a substantial improvement in the interlaminar shear strength. Wertheimer and Schreiber[18] treated aramid fabrics with allylamine and hexamethyldisiloxane plasma. Using peel tests, they found that the bond strength decreased after treatment with allylamine plasma alone. But when fabrics were first activated in argon plasma before introducing allylamine plasma, bond strength improved measurably. Krishnamurthy and Kamel[19] reported plasma grafting of allylamine onto glass fibers. Although the grafted surface was observed under SEM, the interfacial bond strength was not measured. The allylamine plasma has been found to be polymerizable and useful for preparing reverse osmosis membrane.[20,21]

Advantages for both polymerforming and non-polymerforming plasma treatments are described below. It can be seen that non-polymerforming plasma has advantages in process operations, whereas polymerforming treatment is better in that it has fewer adverse effects on the properties of fibers and composites.

Polymerforming Plasma Treatments

1. Fewer detrimental effects on fiber strength.
2. Fewer detrimental effects on flexural and impact strength.
3. Availability of a wide variety and functionality of gases and liquids.

Non-Polymerforming Plasma Treatments

1. Easier operation.
2. Lower material cost.
3. Higher safety and less pollution.
4. Does not contaminate the reactor because no film is deposited.

Coating treatments through plasma polymerization have several advantages over other techniques of coating or sizing. First, plasma polymerization is least affected by the chemical nature of the surface or the bulk properties of fibers. Good adhesion of deposition to the fiber surface is generally obtained.[22,23] Since plasma contains electrons and UV light, the substrate surface is activated through the bombarding of electrons and UV irradiation. The activated surface can then react with the depositing polymer. Yasuda and coworkers[23] also suggested an atomic interfacial mixing mechanism. They proposed that the activated species can diffuse a few atomic monolayers into the substrate surface and become the seed sites for polymer growth, resulting in grafting of the polymer film onto the fiber surface. Second, polar groups such as amino, carbonyl, and hydroxyl groups can be incorporated onto the deposited film by choosing the appropriate monomers and by exposing to them appropriate chemical environments after the plasma treatment. As a result of the polar groups, surface energy, and hence the wettability, increases significantly. Furthermore, plasma polymerized films are highly cross-linked and hence thermally stable, which is evident from DSC and TGA analysis.[24,25]

In the present study, the surface of UHSPE fibers was modified through allylamine plasma polymer deposition. The effects of plasma treatments on fiber/epoxy interface and fiber mechanical properties were investigated.

EXPERIMENTAL

Materials

UHSPE fiber, Spectra 900, with a nominal fiber diameter of 38 μm, was obtained from Allied Fiber Company in the form of yarn containing 118 filaments. The fiber properties have been given earlier in Table I. Allylamine ($H_2C = CHCH_2NH_2$), 98% purity, was obtained from Aldrich Chemical Corporation, and was distilled before being used for plasma polymerization. Epoxy resin, DER 331, and curing agent, DEH 26, were used for this study. DER 331 is a diglycidyl ether of bisphenol A (DGEBA) with an average epoxy equivalent weight (EEW) of 187. DER 26 is a tetraethylene pentamine (TEPA) with amine hydrogen equivalent weight (AHEW) of 27.1. Both epoxy resin and curing agent were obtained from Dow Chemical Company.

Specimen Preparation for Plasma Treatment

Two yarns of Spectra 900 fibers were wound on an aluminum frame (150 mm $\times$ 50 mm). The ends were

glued to the frame using epoxy resin. After the epoxy was cured, the fibers on the frame were washed with methanol solvent for 15 min and dried in a vacuum oven at 60°C for 30 min. Aluminum frames, with fibers, were then kept in desiccators until the plasma treatment.

Thin glass cover slides, used in optical microscopy, were used for the contact angle measurement after being cleaned with acetone.

Plasma Polymerization Treatment

The plasma polymerization of allylamine was carried out using a Plasma Discharge System (PDS), Model 504, manufactured by LFE Corporation. The equipment and experiment have been described in detail in Part I of this study.[26] All treatments were run at a pressure of 500 millitorrs.

Contact Angle Measurement

The contact angle (θ) of water on glass slides was measured by a Contact Angle Analyzer Model CAA2, manufactured by IMASS Inc. Three liquids, water, formamide, and benzyl alcohol, with surface tensions of 72.75, 58.3, and 40.9 dyne/cm^2, respectively, were used for obtaining Zisman's plot[27] to measure the critical surface tension of the deposited films.

Fiber Tensile Test

Single filaments were tension tested on an Instron tensile testing machine Model 1122. Data were collected on a Hewlett-Packard computer mode 86B. Before each test, the cross-sectional area (A) of individual fiber was measured using a vibroscope according to ASTM D1577–79.[28] The fiber density was assumed to be 0.97 g/cm^3. This cross-sectional area was used to calculate the fracture stress.

The filament was then wound on capstan jaws as described by Schwartz et al.[29] Jaw spacing (apparent gauge length) of 50 mm and a cross-head speed of 5 mm/min was used. In order to calculate the effective gauge length, after compensating for the contribution to elongation from the wound part of the fiber, the following procedure was adopted. The fiber was marked at two points, A and B, by tying two knots as shown in Figure 1. The fiber was then strained to approximately 80% of the breaking elongation at the same cross-head speed as used for the
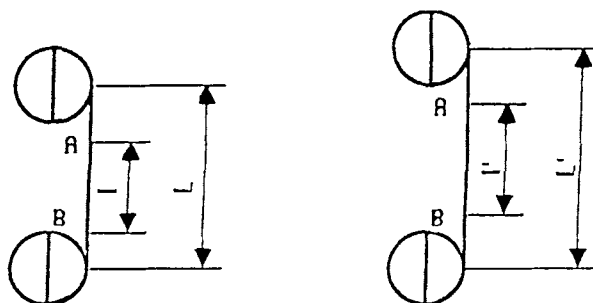

Figure 1 Schematic for calibration of effective gauge length.

tensile test. The effective gauge length, L_{eff} was obtained using the following equation:

$$(L' - L)/L_{\text{eff}} = (l' - l)/l \qquad (1)$$

The effective gauge length was found to increase with the number of loops wound on the capstan jaws until a certain number was reached. Three and three quarters (3.75) loops were wound on the capstan jaws for every test to keep a constant effective gauge length. The fiber moduli were calculated using the effective gauge length instead of the apparent gauge length (L). Twenty five tension tests were performed for each experimental condition. Two parameter Weibull distribution was fit to the strength data. Estimates of Weibull parameters were obtained using the method of maximum likelihood estimation (MLE).[30]

The T-test was used to discern the effect of various treatments on the mechanical properties. For testing the difference between the effects of power and time on mechanical properties of fibers, a one-way analysis of variance was performed. A confidence level of 95% was used for all tests.

Single-Fiber Pull-Out Test

Silicone rubber molds were specially made, as shown in Figure 2(A), using RTV 664 obtained from General Electric Company. A slit was cut up to half the depth of the cavity, perpendicular to the mold. Thus, when the silicone mold was bent, the slit could open to form a V-shaped crack. A single filament was then placed in the crack. When the mold was released, the crack closed. A small spring was attached to the fiber when it was placed in the crack to keep the fiber under slight tension in the mold. Care was taken to prevent the fiber from sliding in the slit, and to prevent any surface contamination. This is
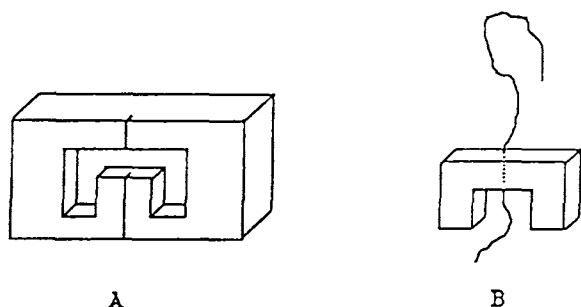
Figure 2 (A) Silicone rubber mold, (B) Epoxy resin specimen with embedded fiber ready for single-fiber pull-out test.

especially important if the molds are coated with a silicon mold release agent.

The DER 331 epoxy resin and DEH 26 curing agent, both obtained from Dow Chemical Company, were mixed thoroughly in stoichiometric proportion. The mixture was degassed in a vacuum oven. The mold was then filled with the mixed epoxy resin slowly without disturbing the fiber. The epoxy resin was cured in the mold for 3 h at 80°C and was post-cured for an additional 1 h at 110°C in oven, after which air was let in. Single-fiber pull-out specimens, thus prepared, were taken out of the silicone mold [Figure 2(B)].

The lower part of the fiber, protruding out of the epoxy resin specimen, was sheared using a razor blade. To conduct a single-fiber pull-out test, the upper part of the fiber was wound on the same capstan jaw as was used for the tension tests, which was clamped in the upper clamp of Instron. Three and three quarters (3.75) loops were wound on the capstan jaw each time. Schematic of the single-fiber pull-out test set-up is shown in Figure 3. The pull-out test was run on Instron at a cross-head speed of 1 mm/min. Care was taken to align the fiber perpendicular to the epoxy resin. The free fiber length, L, illustrated in Figure 3, was equal to 100 mm. The elongation of the fiber is defined as $\delta L / L$, where δL is the displacement of the upper clamp. Load vs. elongation of the fiber was plotted.

Before placing the fiber in the crack of the mold, the cross-sectional area of each fiber was measured using the vibroscope technique, as described earlier. Average interfacial shear strength (τ) was obtained using the following formula:

$$\tau = F_p/\pi dl \qquad (2)$$

where F_p is the fiber pull-out load as illustrated in Figure 8, d is the fiber diameter, and l is the embed-

ded fiber length. Eight to ten tests were run for each experimental condition.

Hot Water Immersion Effect on Pull-out Test

The single-fiber pull-out specimens were immersed in distilled water at 70°C for 5 h and then were transferred to a container containing room temperature tap water for 15 min. After removing them from water, the specimens were wiped dry with tissue. Single-fiber pull-out tests were conducted as described above. Ten tests were performed for each condition.

Surface Characterization by Scanning Electron Microscopy (SEM)

Surface topography of control and treated fibers, as well as the fibers pulled out from epoxy resin, were studied by a scanning electron microscope model JOEL JSM 35CF. After coating with 60/40 gold/palladium alloy, an accelerating voltage of 10 KV was used throughout the study. It was found that the UHSPE fibers were very easily damaged by the electron beam radiation in the SEM. To prevent the damage, the current was maintained as low as possible. Fibers also had to be coated several times by placing them at different angles to prevent charging.
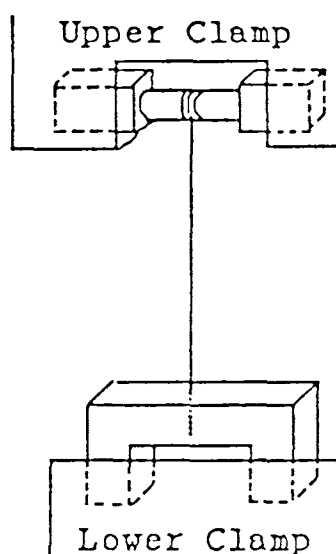

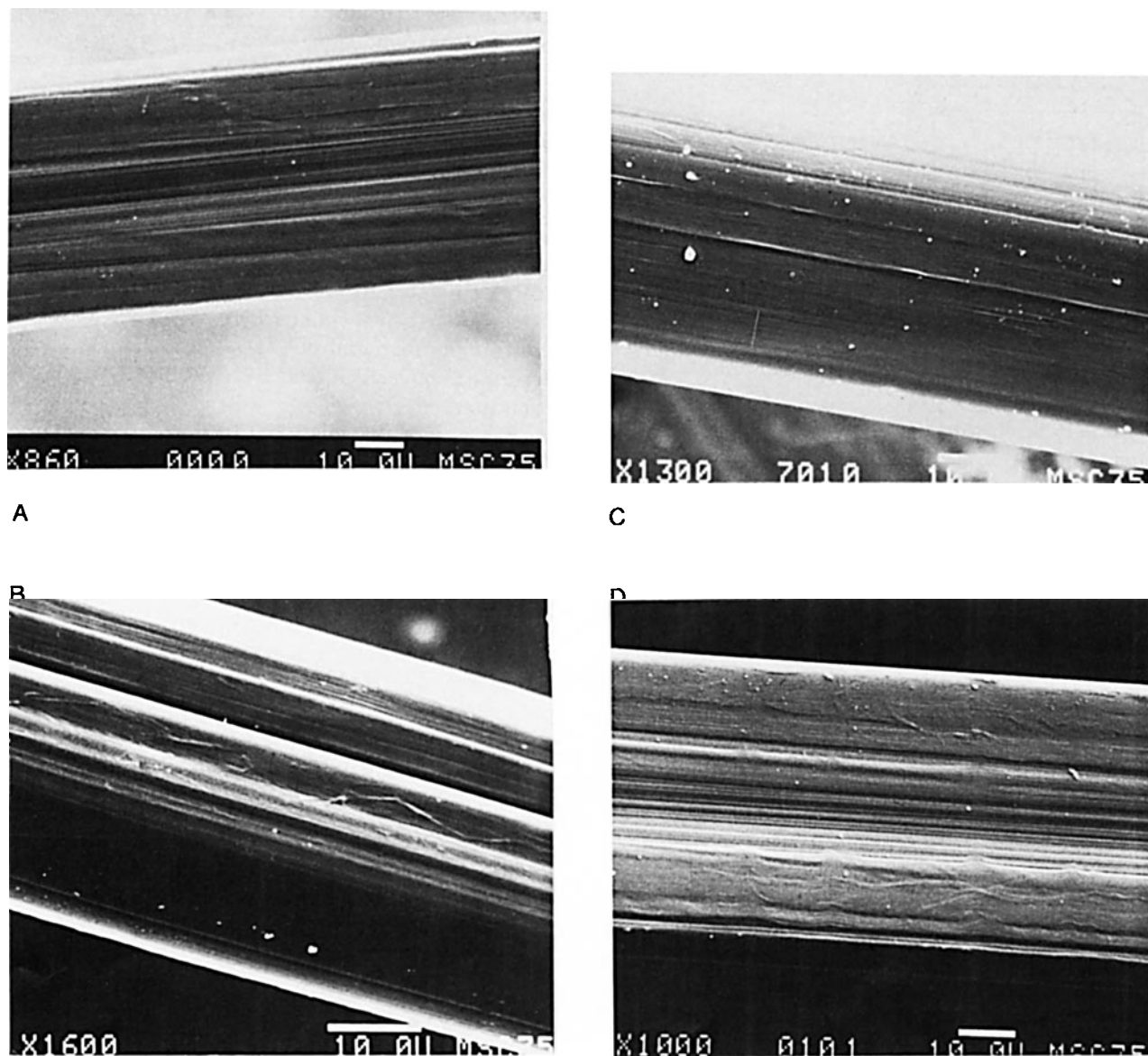**Figure 3** Schematic of single-fiber pull-out test.

Figure 4 SEM Micrograph of UHSPE fiber surface. (A) Control and allylamine plasma treated at (B) 30 W, 10 min, (C) 70 W, 10 min, (D) 45 W, 40 min.

RESULTS AND DISCUSSION

Fiber Surface Topography

The SEM photomicrographs of untreated and treated fiber surfaces are shown in Figure 4(A–D). No change in the surface texture can be detected after treating at 30 W and 45 W for 10 min. The thickness of the polymer coating, as measured on silicon wafers, is less than 500 Å.[26] At the higher power input of 70 W, a few particles were found on the fiber surface, as shown in Figure 4(C). Since

the rate of polymerization is high at 70 W, polymers can aggregate to form powders before depositing onto substrates. Krishnamurthy and Kamel,[19] who coated the glass fibers with allylamine plasma at 150 W for 10 min, observed fairly thick, powderlike depositions on glass fibers. Powder was also deposited on the fiber surface at longer exposure times. In the present case, powder particles were found exclusively on the left end of the reaction chamber from where the monomer was introduced. A few fine powder particles were also seen to have drifted towards other parts of the chamber and substrates.
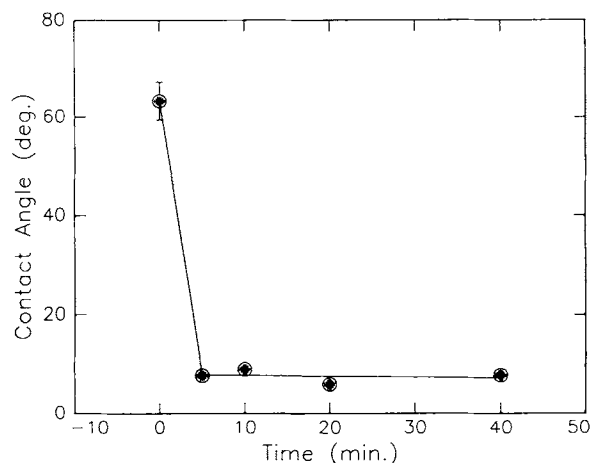
Figure 5 Contact angle of water on glass slide as a function of treatment time.

Figure 6 Contact angle of water on glass slide as a function of power input.

Figures 5 and 6 show changes in contact angle on glass slide, using water, as a function of plasma polymerization time and power input, respectively. As seen in Figure 5, contact angle drops dramatically from 63.4° for control specimen to 7.8° for allylamine plasma polymer film obtained at 45 W for 5 min. Beyond the initial exposure time of 5 min, any increase in time does not change the contact angle significantly. This is presumably because the glass slide gets a sufficient polymer coating in the initial 5 min to change the contact angle. Any further increase in time only increases the film thickness, but not the chemical compositions, and hence produces no further change in the contact angle. As the power increases from 0 W to 70 W, the contact angle decreases almost linearly from 63.4° to 0°, as shown in Figure 6. This is presumably because of the different chemical structure obtained at 70 W than that obtained at lower power input, which is more polar in nature. Contact a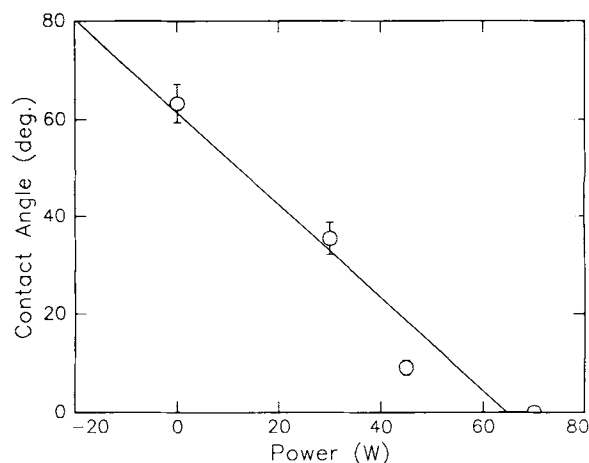ngle of liquid on a solid surface depends on the surface tension of the liquid. If the surface tension of the liquid is below a critical value, the contact angle is zero. Zisman's plot, as shown in Figure 7, is used to obtain the critical surface tension of the deposited polymer films.[27] Critical surface energy increases from 22.5 to 58.0 dyne/cm^2 after the glass slide is deposited with allylamine plasma polymer at 30 W for 10 min. The increase in wettability is due to the polar groups incorporated into the deposition as shown by IR and ESCA in the previous part of this study series.[26]

Results of Single-Fiber Pull-Out Tests

Typical load vs. elongation plots of single-fiber pull-out tests are shown in Figure 8. It can be seen that load increases linearly in the initial part of the plot. Specimens observed under polarized optical microscopy suggested that the interface fails progressively from top to bottom during this period. When

Table III   Results of Single-Fiber Pull-Out Tests

| Treatment Condition	IFSS (CV) (MPa) (%)	Improvement	Specific Energy (Kg/mm^2)	Debonding Rate (mm/min)	Maximum (CV) Friction (g) (%)
Control	0.56 (13.4)	—	46.43	5.0	39.6 (14.6)
30 W 10 min	1.82 (10.9)	3.25	98.82	1.5	79.5 (20.5)
45 W 10 min	1.73 (11.7)	3.09	77.88	1.5	58.7 (23.4)
70 W 10 min	1.64 (25.1)	2.93	96.58	1.7	76.9 (41.4)
45 W 5 min	1.54 (11.8)	2.75	100.96	1.8	67.6 (40.6)
45 W 10 min	1.73 (11.7)	3.09	77.88	1.5	58.7 (23.4)
45 W 20 min	1.25 (21.6)	2.23	97.46	2.1	61.1 (31.5)
45 W 40 min	1.68 (19.2)	3.00	105.97	1.8	81.6 (22.6)
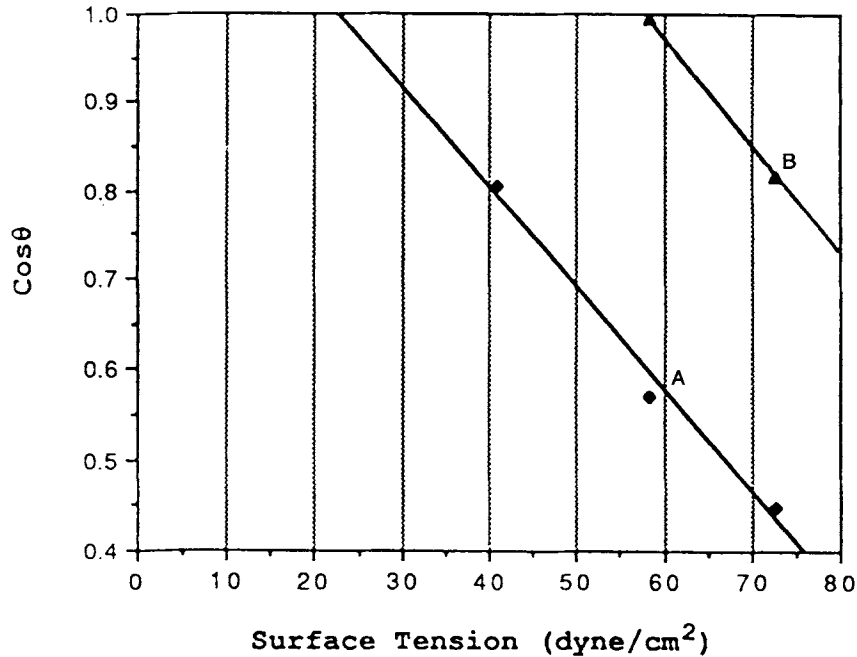
Figure 7   Zisman's plot of critical surface tension of glass slides. (A) Control, (B) Treated with allylamine plasma at 30 W for 10 min.

the fiber debonding process is complete, the fiber slips instantaneously, relieving stress, as shown in Figure 8. The load then rises slowly, until the fiber starts gradually slipping again, and then decreases as the embedded length decreases.

The average rate of debonding, v, can be defined as follows:

$$v = l/t \tag{3}$$

where l is the embedded length of the fiber in epoxy resin and t is the time required for the entire fiber to debond. This is represented by the time to reach the initial peak p in Figure 8. Specific energy, ω, which is the total energy per unit interface area, was obtained by the following formula:

$$\omega = Q/U \times l \tag{4}$$

where Q is the area under the pull-out curve, U is perimeter of fiber. The specific energy, ω, includes the debonding energy as well as the frictional energy.

In Table III we present the average interfacial shear strength (IFSS), specific debonding energy, debonding rate, and maximum friction. Significant improvement in interfacial shear strength is obtained for fibers treated for all different operating parameters over untreated fibers by a factor of 2 to

3. The average debonding rate reduces dramatically from 5.0 mm/min for control fibers to an average of 1.7 mm/min for plasma-treated fibers, indicating much slower debonding for treated fibers. Although the IFSS values are small compared with values obtained for other fibers, such as Kevlar and glass fibers,[31,32] the improvement is significant. One im-
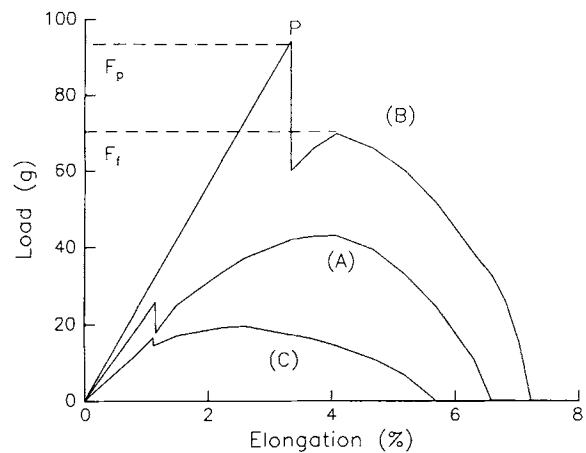

Figure 8   Typical load vs. elongation plots of single-fiber pull-out tests from epoxy resin for (A) Untreated fiber, (B) Treated fiber, (C) Hot water immersed specimen with an untreated fiber.

Table IV   Effect of Hot Water Immersion on Interfacial Bonding Properties

		Control			Plasma Treated at 30 W and 10 min		
		Before Immersion	After Immersion	Percent Retained	Before Immersion	After Immersion	Percent Retained
IFSS	(MPA)	0.6	0.4	66.1	1.8	1.4	78.6
Spec. energy	(Kg/mm²)	46.4	26.1	56.4	98.8	106.7	108.0
Max. friction	(g)	39.8	24.8	62.6	79.5	71.0	89.3

portant factor is the presence of polar groups, which makes fibers wettable by liquid epoxy resins. It can also be seen from Table III that the interfacial shear strength does not change significantly with power input. However, a slight decrease in IFSS at higher power may be due to the reduction in the concentration of primary amines, which are converted to secondary or tertiary amines or imines.[26] Tertiary
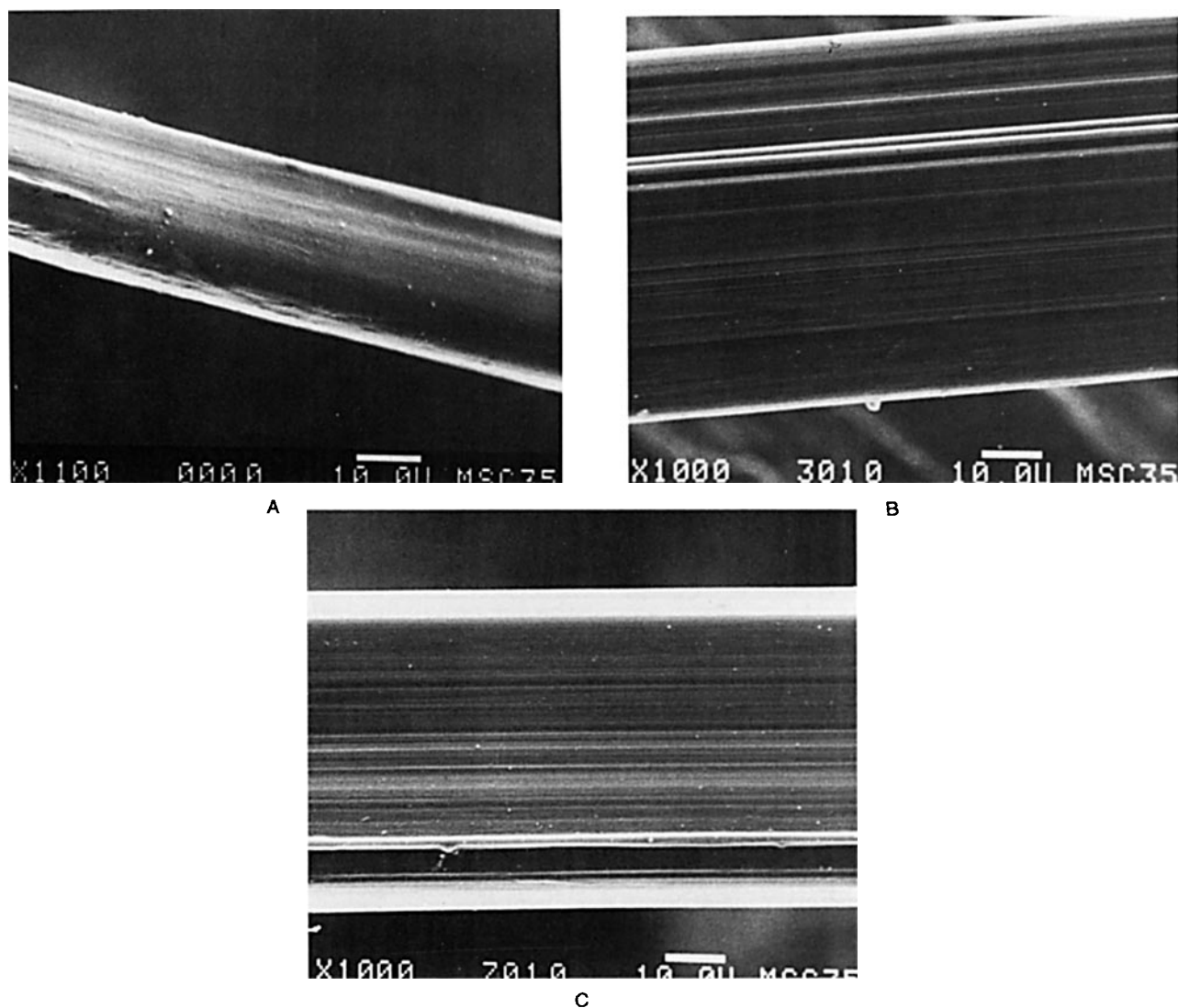

Figure 9   SEM micrograph of pulled-out fiber surfaces, (A) Control and allylamine plasma treated at (B) 30 W, 10 min, (C) 70 W, 10 min.
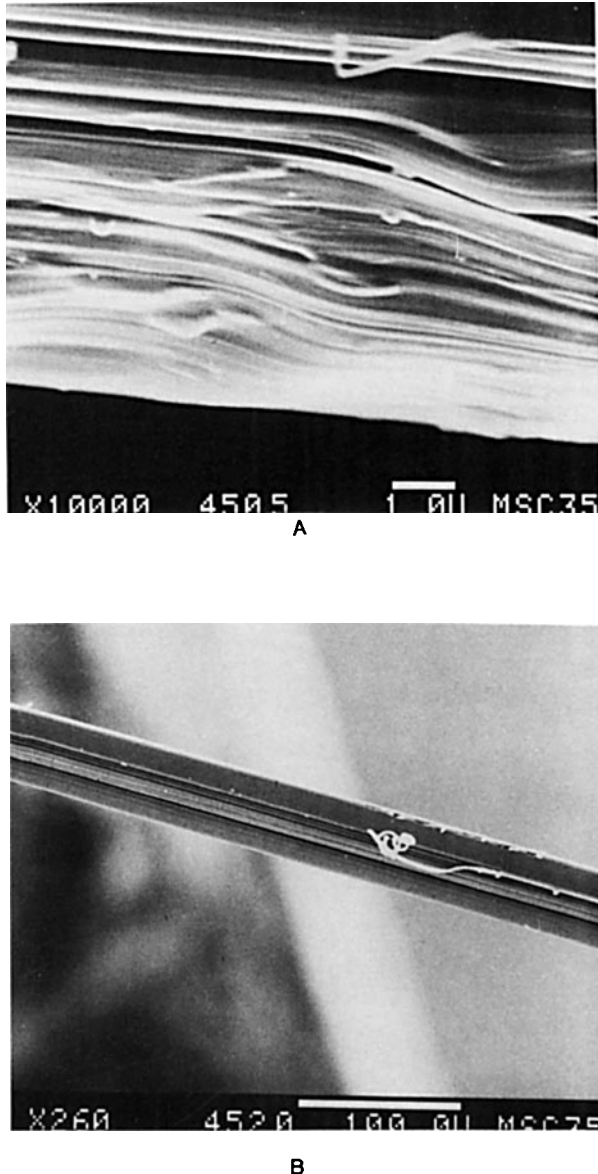
Figure 10 SEM micrograph of pulled-out fiber surfaces treated with allylamine plasma at (A) 45 W for 5 min, (B) 45 W for 20 min showing the fibrillation.

amines and imines do not react with the epoxy resin as primary amines do, resulting in lower IFSS value. At a constant 45 W power input, the IFSS increased from 1.54 MPa to 1.73 MPa for the exposure time of 5 and 10 min, respectively. Further increase in exposure time reduces the IFSS to 1.25 MPa for 20 min and 1.68 MPa for 40 min, showing no clear trend. Quantitative measurement of primary amine concentration on ammonia plasma-treated aramid fiber surfaces was done by Allred et al.[10] Their results showed that the primary amine concentration in-

creased rapidly, reaching a maximum value at a treatment time of 1 min, remained constant until 10 min, and then decreased for longer exposures above 10 min. At longer times, some powder particles may deposit on fiber surfaces as discussed earlier, reducing the interfacial strength. However, at higher power levels when the concentration of polymer particles is higher and if these particles are embedded in the polymer film, the surface roughness may tend to increase the IFSS due to mechanical interlocking. The maximum friction load, F_f, as shown in Figure 8, of treated fibers also increases to almost twice as high as that of untreated fibers.

Effect of Hot Water Immersion on Interfacial Bond Properties

Table IV shows the effect of hot water immersion on the interfacial bond properties. The typical load–elongation curve of single-fiber pull-out tests after hot water immersion is shown in Figure 8(C). It can be seen from Table IV that bonding at the interface between the fibers and epoxy resins deteriorated after specimens were immersed in hot water for 5 h at 70°C. The drop in IFSS is less significant for plasma treated fibers than for untreated fibers. The decrease in IFSS results primarily from the swelling of the specimen due to the moisture diffusion. Moisture may reach the interface, destroying van der Waals forces and hydrogen bonds. Further, the epoxy resin has a higher thermal expansion coefficient than the fiber in the longitudinal direction. At higher immersion temperature, the expansion of the matrix is sufficient to weaken the interface by reducing compressive forces exerted by epoxy resin on the fibers after high temperature curing. Table IV also shows that the maximum interfacial friction is reduced considerably after hot water immersion.

Surface Characteristics of Fibers Pulled out from Epoxy Resins

Figure 9(A–D) shows SEM photomicrographs of fibers pulled out from epoxy resins. Most fiber surfaces are clean. The polymer powder particles that were seen on treated fibers presumably get embedded in matrix and hence stay in the matrix. Figure 10(A) and (B) shows that the interfacial debonding occurs at the interface between the fiber and epoxy resins. In some cases fibrils were peeled from fibers, suggesting that the adhesion at the interface between

Table V   Effect of Allylamine Plasma Treatments on Fiber Strength

Fiber Treatment	Mean Strength (MPa)	C.V. (%)	Scale Parameter (MPa)	Shape Parameter	t-Test[a] Statistic	Significance
Control	3530	6.3	3635	16.7	—	—
30 W 10 min	3441	8.3	3566	15.2	1.2	No
45 W 10 min	3274	11.1	3432	10.1	3.0	Yes
70 W 10 min	3152	10.9	3289	11.6	4.5	Yes
45 W 5 min	3375	9.9	3530	9.8	1.9	No
45 W 10 min	3274	11.1	3432	10.1	3.0	Yes
45 W 20 min	3478	8.1	3609	12.3	0.7	No
45 W 40 min	3319	9.6	3460	11.9	2.7	Yes

[a] The critical value of t-statistic is 2.0 at 95% confidence level for 48 degrees of freedom.

fiber and epoxy resin in some cases may exceed that of interfibrillar forces. It is, however, possible that fibrillation may have been initiated at the pre-existing fiber defect.

Effect of Plasma Treatments on Fiber Strength

The effects of allylamine plasma treatments on fiber mechanical properties are reported in Table V.

Weibull probability plots for fiber strength are shown in Figures 11 and 12. Two parameter Weibull distribution, as shown in Eq. 5, had been used for strength of UHSPE fibers[29]:

$$F(X) = 1 - \exp[-(X/X_0)^\rho]$$

$$X > 0 \text{ and } X_0, \rho > 0 \quad (5)$$
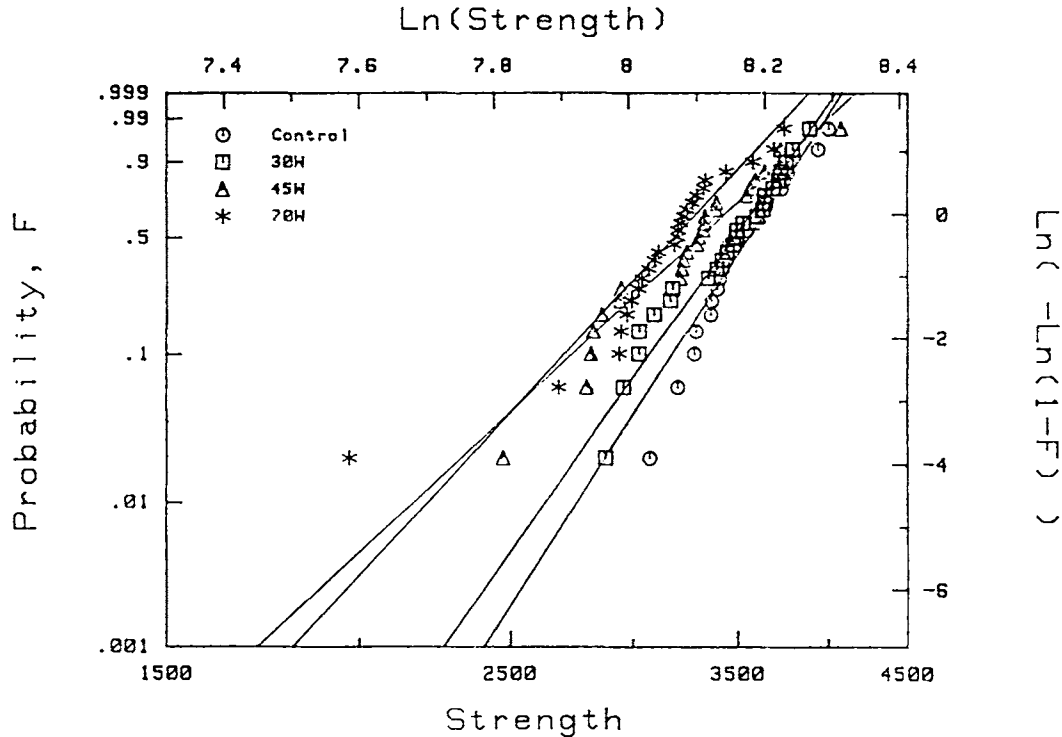

Figure 11   Weibull probability plots of strength of UHSPE fibers treated at different power inputs for 10 min.
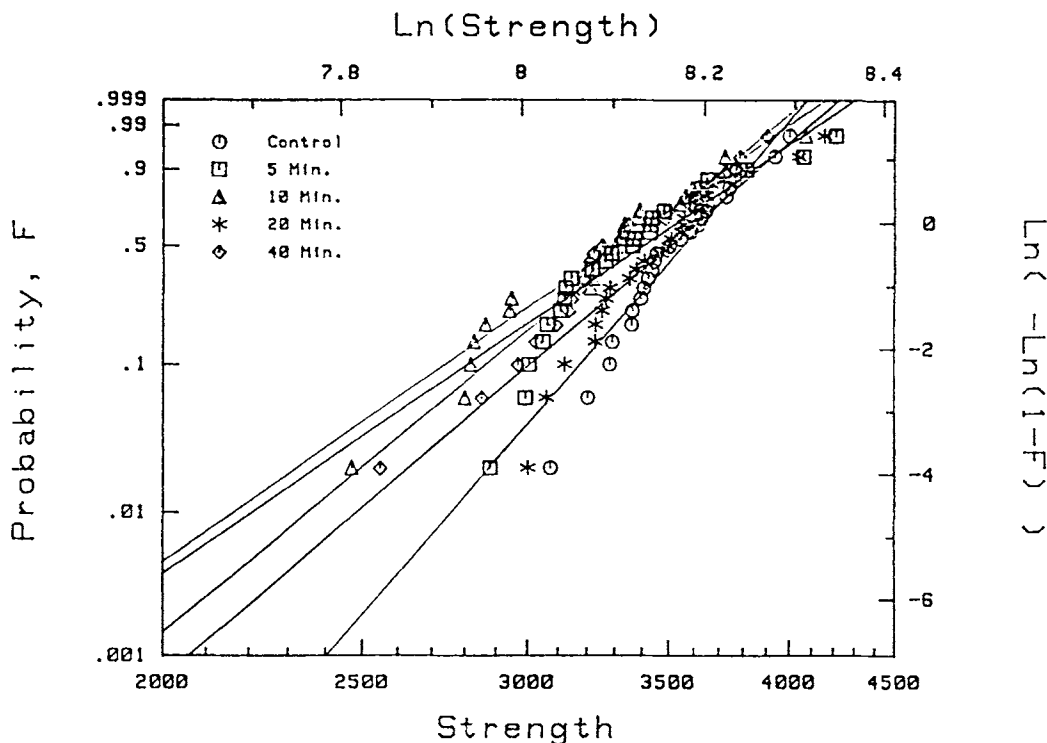
Figure 12 Weibull distribution plots of strength of UHSPE fibers treated at different exposure times at 45 W.

where X is fiber strength, X_0 is the scale parameter, and ρ is the shape parameter. It can be seen from Table V that fiber strength decreases monotonically with power. In the glow discharge plasma, the fibers are subjected to UV radiation and electrons, which may cause chain scissions or crosslinks and defects in crystalline regions. The author found severe defects in crystalline regions and even destruction of

some forms of crystallites when the UHSPE fibers were exposed to ^{60}Co γ-rays in air at 6 Mrads per dose. Klein et al.[33] also showed that chain scissions were predominant over cross-linking in UHMPE fibers irradiated in vacuum or in acetylene. The analysis of variance showed a significant effect of power input on fiber strength. Although the strength is lowered for all exposure times at constant power

Table VI   Effect of Plasma Treatment on Fiber Fracture Strain and Initial Modulus

Fiber Treatment	Strain (%)	C.V. (%)	t-Test Statistic	Significance	Initial Modulus (GPa)	C.V. (%)	t-Test Statistic	Significance
Control	5.32	7.8			58.7	21.5		
30 W 10 min	5.88	10.2	3.8	Yes	61.2	16.6	0.8	No
45 W 10 min	4.90	10.3	3.2	Yes	67.5	18.5	3.2	Yes
70 W 10 min	5.19	11.4	0.9	No	65.1	22.0	1.6	No
45 W 5 min	5.35	9.5	0.2	No	61.2	14.4	0.8	No
45 W 10 min	4.90	10.3	3.2	Yes	67.5	18.5	3.2	Yes
45 W 20 min	5.11	6.7	1.9	No	66.5	14.9	2.4	Yes
45 W 40 min	5.16	11.9	1.1	No	64.9	18.4	1.8	No

input of 45 W, analysis of variance showed that the decrease in strength due to time is statistically not significant.

Table VI shows the effects of the treatments on fracture strain and the initial modulus of fibers. Although the initial modulus is not affected, the values for all treatments are higher than control specimens. One-way analysis of variance shows that the fracture strain is affected by power input as well as the exposure time. The trend, however, is not clear. The increase in the initial modulus, combined with the changes in the fracture strain, suggests that the fiber may be getting slightly brittle after plasma treatment. This suggestion supports the results obtained by Klein et al.[33] in that significant gelation occurred as a result of electron beam irradiation of the UHMPE in acetylene environment.

CONCLUSIONS

1. The allylamine plasma can give a thin coating on the UHSPE fibers. No change in surface topography of the fibers was observed, however, at higher power input and at longer exposure times a few polymer particles were found.
2. Contact angle of allylamine plasma deposited film at 45 W power input for 5 min dropped from 63.5° to 8°, but any increase in time, beyond the initial 5 min, did not decrease the contact angle further. With the increase in the power input, the contact angle decreased almost linearly, and became zero at 70 W.
3. The interfacial shear strength (IFSS) increased dramatically for UHSPE fibers for all treatment times and power. Maximum IFSS was obtained for fibers treated at 30 W for 10 min. The IFSS value decreased slightly with the increase in power input. No such trend was found in IFSS value as a function of treatment time.
4. Surface topography of most fibers pulled out from epoxy resin showed clean fiber surfaces. In a few cases, fibrils were peeled from fibers, indicating the possibility of higher interfacial strength than the interfibrillar attraction or pre-existing fiber defect.
5. Fiber strength decreased, but initial modulus increased after plasma treatments. Analysis of variance showed that power input had a significant effect on fiber strength, whereas

treatment time had no significant effect. The decrease in strength at lower power input, 30 W, was, however, not significant.

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