

Surface Modification of Ultra High Modulus Polyethylene Fibers by an Atmospheric Pressure Plasma Jet

T. Wang,^{1,2,3} C. Wang,^{1,2,3,4} Y. Qiu^{1,2,3}

¹State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, China

²Key Laboratory of Textile Science and Technology, Ministry of Education, China

³Department of Textile Materials Science, College of Textiles, Donghua University, Songjiang, Shanghai 201620, China

⁴College of Textiles and Clothing, Yancheng Institute of Technology, Jiangsu 224003, China

Received 14 November 2005; accepted 30 November 2006

DOI 10.1002/app.26738

Published online 21 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To improve their adhesion properties, ultra high modulus polyethylene (UHMPE) fibers were treated by an atmospheric pressure helium plasma jet (APPJ), which was operated at radio frequency (13.56 MHz). The surface properties of the fibers were investigated by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and contact angle measurement. The surface dyeability improvement after plasma treatments was investigated using laser scanning confocal microscopy (LSCM). The adhesion strengths of the fibers with epoxy were evaluated by microbond tests. In addition, the influence of operational parameters of the plasma treatment including power input and treatment temperature was studied. XPS analysis showed a significant increase in the surface oxygen content. LSCM results showed that the plasma treatments greatly increased fluorescence dye con-

centrations on the surface and higher diffusion rate to the fiber center. The tensile strength of UHMPE fiber either remained unchanged or decreased by 10–13.6% after plasma treatment. The contact angle exhibited a characteristic increase in wettability, due to the polar groups introduced by plasma treatment. The microbond test showed that the interfacial shear strengths (IFSS) increase significantly (57–139%) after plasma treatment for all groups and the optimum activation is obtained at 100°C and 5 W power input. SEM analysis showed roughened surfaces after the plasma treatments. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 25–33, 2008

Key words: atmospheric pressure plasma jet; interfacial strength; laser scanning confocal microscope; UHMPE fibers

INTRODUCTION

Ultra high modulus polyethylene (UHMPE) fiber is a high performance fiber made from ultra high molecular weight polyethylene (UHMWPE) by gel spinning/hot drawing process.¹ UHMPE fiber has been widely used in composites since it offers many desirable properties, such as high tensile strength, high tensile modulus, and good abrasion resistance. Moreover, this kind of fiber has excellent impact energy absorption capability and UHMPE fiber composites are used for ballistic resistant parts.^{2,3} However, the chemical inertness and low surface energy of UHMPE makes it hard to achieve good adhesion,

and limit the applications of the fiber in composites. Consequently, extensive researches have been conducted to modify the surface of UHMPE fibers.^{4–9} Among various surface treatment techniques, plasma treatment is one of the most effective ways.

Plasmas operated at atmospheric pressure have been successfully used to improve the bondability^{4,6,10–14} and wettability^{12,15–17} of polymers by introducing polar groups or creation of the surface roughness^{18–22} without affecting the bulk properties. Typical atmospheric pressure plasma systems are corona discharges and dielectric barrier discharges. Recently an atmospheric pressure plasma jet is available.²³ It has advantages of low temperature, uniform treatment, versatile treatment gases, and adjustable power input and gas flow rate. Little has been reported in published literature regarding to the effect of atmospheric pressure plasma jet (APPJ) on improving adhesion between UHMPE fiber and any resins used in composites. In this study the modifications of UHMPE fibers surface using an APPJ system were evaluated. In addition, the influence of variation of process parameters on the activation results was also studied.

Correspondence to: Y. Qiu (ypqiu@dhu.edu.cn).

Contract grant sponsor: Program for Changjiang Scholars and Innovative Research Team in University; contract grant number: IRT0526.

Contract grant sponsor: Shanghai Pujiang Program; contract grant number: 06PJ14011.

Contract grant sponsor: Donghua University.

Journal of Applied Polymer Science, Vol. 108, 25–33 (2008)

© 2007 Wiley Periodicals, Inc.

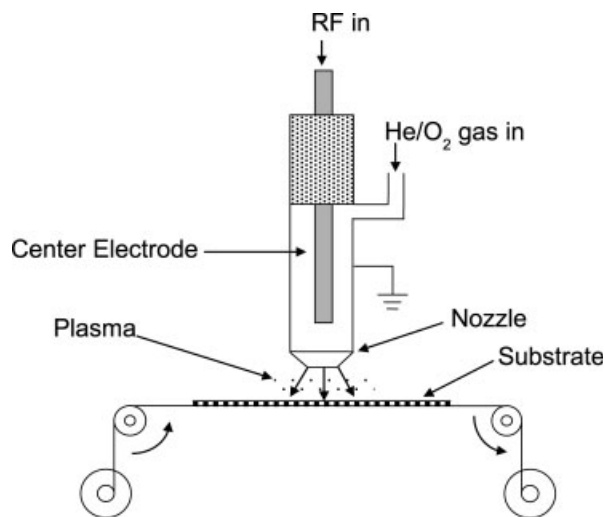


Figure 1 Schematic of the atmospheric pressure plasma treatment device.

Plasma treatment can also improve the dyeability of fibers.^{24–26} Park and Jin treated low-density polyethylene films with a radio frequency corona discharge apparatus and found that after the treatment the K/S value of dyeability increased when a basic dye was used.²⁷ Ferrero, who polymerized acrylic acid on polypropylene fabrics, obtained similar results.²⁸ The improvement of dyeability by plasma treatments has been attributed to the improved surface wettability and affiliation to dye molecules. Therefore the improvement on dyeability is also an indication of surface modification effects. However, traditional way to detect the improvement of dyeability of a fiber like UHMPE is extremely difficult if not impossible since the fiber cannot be dyed in conventional dyeing processes. Laser scanning confocal microscope (LSCM) has been used to study the microscopic dye diffusion process in nylon fibers^{29–32} in which, 3D images of fluorescent dyed fibers can be obtained without destroying the specimens. Therefore, in this research, LSCM was employed to detect the dye adsorption to the surface of UHMPE fibers as an indication of the effect of the plasma treatments.

EXPERIMENTAL

Materials

The UHMPE fibers employed in the experiments were provided by Ningbo Dacheng Company (Zhejiang, China). The average diameter of the fiber was $29.4 \pm 1.8 \mu\text{m}$. The matrix was epoxy resin prepared with DER 311 (bisphenol-A type epoxy) and DER732 (polyglycol diepoxide) and the curing agent was DEH26 all supplied by Dow Chemical.

Plasma treatment

Prior to each plasma treatment, the UHMPE fibers were washed in acetone for 5 min to remove surface contaminants and then were dried in a vacuum oven to eliminate the remaining acetone from the fibers.

The plasma treatments were carried out using an APPJ manufactured by the Surfex Technologies LLC, USA. Figure 1 shows the schematic of the APPJ treatment system. This device employs a capacitively coupled electrode design and produces a stable discharge at atmospheric pressure with 13.56 MHz radio frequency power and constant helium gas flow. The helium gas was 99% pure and flowed at a rate of 10 L/min. The plasma jet system with a nozzle mounted above a moving belt and covered an active area of $2 \times 10 \text{ mm}^2$. The fibers moved underneath the plasma jet at a speed of 2.2 mm/s. This was fulfilled by a winding system that was able to control the moving velocity of the fiber. The process conditions of the plasma treatment are given in Table I. The plasma treatment head was heated by an internal heater to the predesignated temperatures to vary the treatment effect. After the treatment, the fibers were immediately placed into a clean plastic bag that was then sealed to minimize potential contamination.

Scanning electron microscopy

JSM-5600LV scanning electron microscopy (SEM) system was used to inspect the surface modification of the fibers directly after plasma treatment. The fibers were platinum coated to obtain a conducting layer of less than 100 Å to prevent charging on the surface of the specimens. SEM images were taken at $\times 10,000$ magnification.

X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy (XPS) analysis was used to investigate the surface chemical composition of the fibers before and after the plasma treatments using a MICROLAB MKII X-ray photoelectron spectrometer. The X-ray source was Mg K α , (1253.6 eV) and photo emitted electrons were collected at a take-off angle of 45°. The pressure within the XPS chamber was between 10^{-9} and 10^{-10} torr (10^{-7} and 10^{-8} Pa). Each specimen was scanned five times at

TABLE I
Parameters Used in APPJ Plasma Treatments

Group	1	2	3	4	5	6
Treatment head temperature (°C)	30	30	60	60	100	100
Plasma power (W)	5	10	5	10	5	10

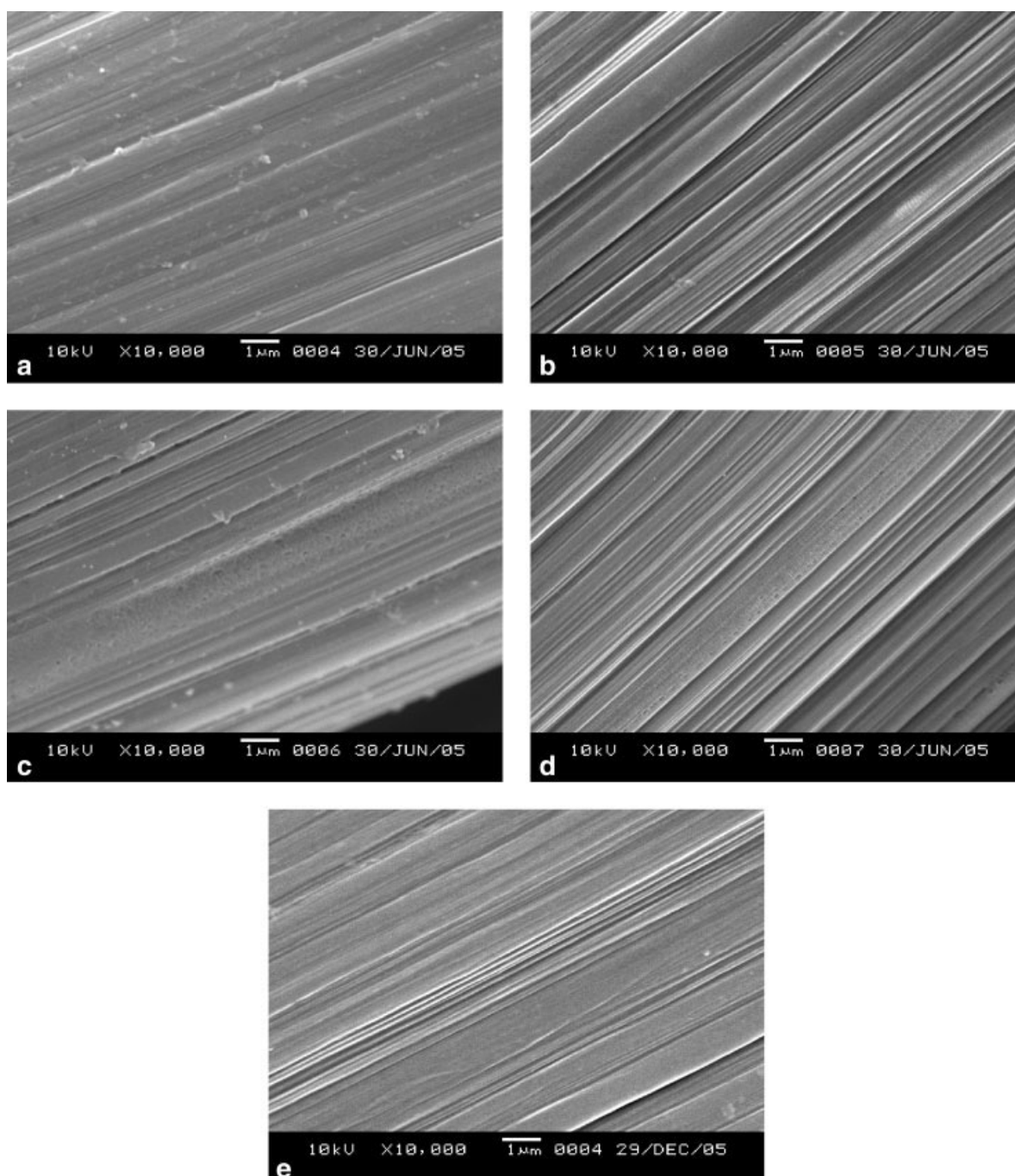


Figure 2 SEM micrographs of UHMPE fibers: (a) 60°C 5 W, (b) 60°C 10 W, (c) 100°C 5 W, (d) 100°C 10 W, (e) control.

0.1 eV/step. The deconvolution analysis of C_{1s} peaks was carried out using XPS Peak software.

Laser scanning confocal microscope

Untreated and treated UHMPE fibers were dyed with propidium iodide fluorescent (0.1 g/L) at room temperature for 30 min. After being washed by distilled water, the fibers were imaged using a LSM 510 META system. It is equipped with a laser system with a wavelength range of 458–1050 nm. The

images were obtained using xy-scan, thus providing an optical cross section of the fiber under study. The images were quantified and analyzed into fluorescent intensity profiles by using Zeiss LSM Image Browser software.

Wettability measurement

Wettability was determined by measuring the contact angles using sessile drop technique by determining the shape of water droplets attached to the fibers

TABLE II
Surface Chemical Compositions of UHMPE Fibers Untreated and Treated with Atmospheric Pressure Plasma Jet Determined by XPS

Treatment	Atomic concentration (%)		% Chemical bonds (binding energy, eV)				
	C	O	C—C (285)	C—OH (286.4)	C=O (288.3)	COOH (289.6)	O=C—O (290.7)
Control	91.1	8.9	86.4	11.4	1.0	0.9	0.3
30°C 5W	90.6	9.4	81.8	13.2	2.9	1.5	0.6
30°C 10W	90.3	9.7	81.1	13.8	3.2	1.2	0.7
60°C 5W	89.9	10.1	80.7	14.1	3.2	1.5	0.5
60°C 10W	91.2	8.8	79.0	15.5	3.3	1.5	0.7
100°C 5W	89.3	10.7	75.4	19.6	3.0	1.5	0.5
100°C 10W	90.1	9.9	80.3	16.1	1.9	1.2	0.5

from digital images taken by a JC2000A Stable contact angle analyzer as described by Carroll.^{33,34}

Sample preparation for microbond test

Immediately after the plasma treatment, the microbond specimens were prepared on a frame as described in literature³⁵ with DER 331 and DER 732 at a ratio of 70 : 30, and 12 phr (parts per hundred resin parts) of hardener DEH 26. After placing the beads on the fibers, the specimens were cured for 3 h at 80°C and postcured for 2 h at 100°C.

The diameters of the fibers and the lengths of the epoxy beads were measured using an Olympus CH-2 microscope equipped with a Panasonic WV-GP410/A digital photomicrography system.

Adhesion measurements

The fiber/resin adhesion was measured with the microbond technique.³⁵ One end of the fiber was attached to the load cell, and a microvise grips the resin droplet and moves downward, shearing the droplet off the fiber. The microbond test was carried out on a Multi Functional Material Tester H5KS-1105 machine at a displacement rate of 1mm/min with a load cell of 50N.

Single fiber tensile test

Single fiber tensile test was performed to inspect the impact of the plasma treatment on fiber strength. The test was carried out at 20°C and 65% relative humidity with a gauge length of 10 mm and cross-head displacement rate of 5 mm/min using a load cell of 50N on a XQ-1 fiber tensile testing machine. The cross section area of the fibers was calculated from their linear densities measured with a XD-1 vibrate linear density machine. At least 20 specimens were successfully tested for each treatment condition.

Statistical analysis methods

One way analysis of variance (ANOVA) and Fisher's pair-wise multiple comparisons were used to compare the tensile strengths of the fibers in different treatment groups. Regression analysis and covariance analysis were used to inspect IFSS and tensile strength of UHMPE fibers among different treatment groups. A P-value less than 0.05 was considered significant.

RESULTS AND DISCUSSION

Surface morphology

SEM images of UHMPE fibers before and after plasma treatment at $\times 10,000$ magnifications are shown in Figure 2. Certain degree of surface roughening or etching is visible for all plasma treated groups.

Hild and Schwartz¹ found when UHMWPE fibers treated with argon plasma for 10 min, the plasma treated samples did not show significant increase in roughness at a magnification of $\times 2000$. The surface roughness shown in the images is at nanometer level and therefore a magnification of $\times 10,000$ or more is definitely necessary. The lengthwise striations observed on the surface were inherent to the fiber.

XPS analysis

Since the UHMPE fiber is nonconductive, the chemical shift of the XPS peaks to higher binding energy was observed due to the surface charging effect. In this case, the C—C bond with the binding energy of 285 eV was used as the reference for calibration.

Table II shows the detailed chemical composition changes on the surfaces of UHMPE fibers. The atomic concentration of oxygen increased slightly for all groups after plasma treatments. And the highest oxygen concentration was observed when the fibers were treated at 100°C and 5 W power input. These

changes are due to the oxidation of the sample surface during plasma processing. Also, a survey scan indicated that no elements other than oxygen were introduced on the UHMPE fibers surface after plasma treatment. Deconvolution analysis of C_{1s} peaks showed an increase in surface hydroxyl groups, which can interact with epoxy resin.

Figure 3 shows the C_{1s} spectrum of the sample surface before and after plasma treatment. The spectrum of untreated sample (A) can be fitted with five peaks. The appearance of little amount of polar groups is attributed to the oxidation of untreated polymer surface when exposed to the air. The C_{1s} spectrums in Figure 3(B) shows additional oxidized species start to appear and the total oxygen abundance also increased. The major peak at 285 eV can be assigned to alkyls (C—C) and other smaller peaks were assigned to C—OH at 286.4 eV, and C=O at 288.3 eV, and COOH at 289.6 eV, and O=C—O at 290.7 eV. The increase of oxygen must have come from the air during the plasma treatment process.

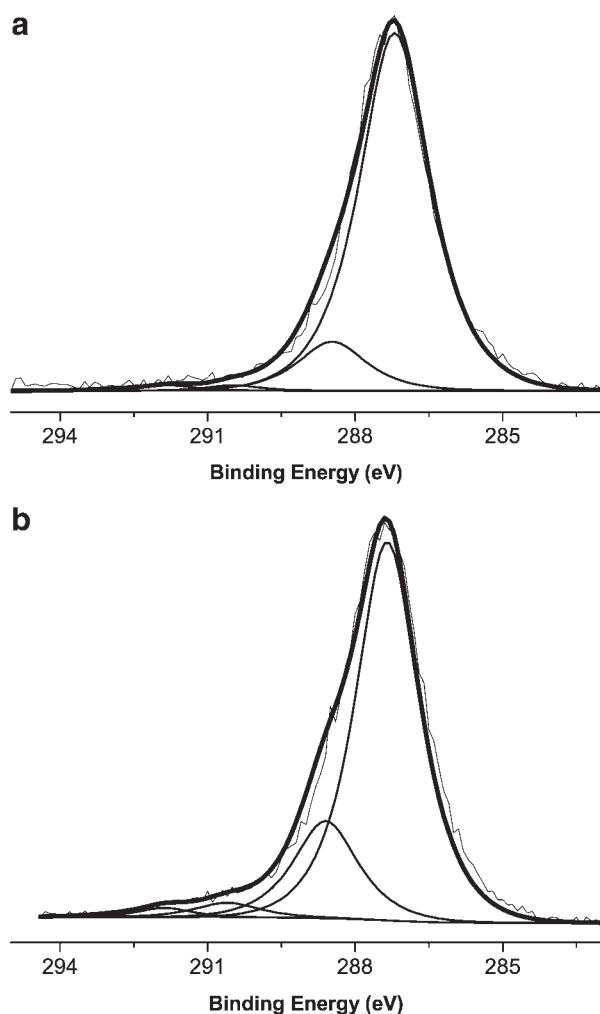


Figure 3 Carbon (1s) XPS spectra for (a) untreated UHMPE fibers and (b) UHMPE fibers treated at 100°C 5 W.

TABLE III
Contact Angles from Wettability Measurements of Distilled Water on Control and Treated UHMPE Fibers

Treatment	No. of specimens	Contact angle	
		Mean	Standard deviation
Control	29	128	6
30°C 5W	15	77	3
30°C 10W	15	73	4
60°C 5W	16	70	4
60°C 10W	14	66	3
100°C 5W	20	70	4
100°C 10W	13	68	5

With increase of temperature and power input, an increase in oxygen atomic concentration was observed. This is accompanied by an increase in polar groups. The highest oxygen atomic concentration obtained was at 100°C and 5 W power input. However, higher power input at 60 and 100°C did not lead to higher oxygen atomic concentration. Similar phenomena were observed by Bhat et al.³⁶ These results are in agreement with results reported in the literature.^{6,7,18,20,37-41}

Wettability measurement

Table III shows the mean contact angles of the control and the plasma treated fibers. To evaluate the influence of the volume of the water droplet on the contact angles, the volume of the droplet were calculated using a method described by Carroll.^{33,34} Covariance analysis was performed on the data to test the effects of power input and temperature holding water droplet volume as the covariance ($\alpha = 0.05$). The results showed that the volume did not significantly affect contact angle ($P = 0.243$) and thus was eliminated in subsequent statistical analysis. The contact angle dropped dramatically from 128° for the

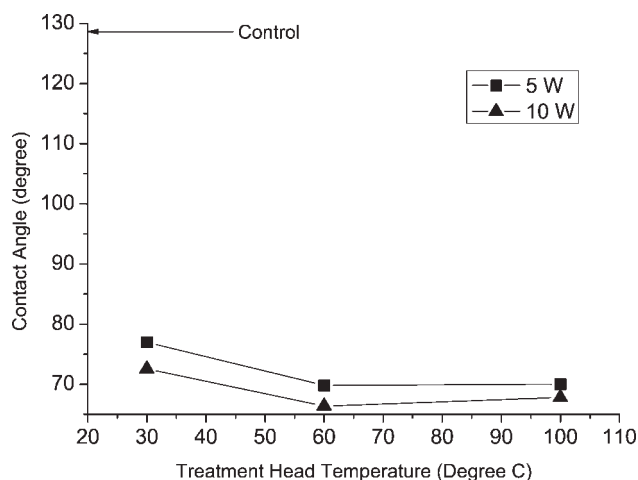


Figure 4 Change in contact angle for He plasma treated UHMPE fibers with treatment head temperature as determined by wettability measurements of distilled water.

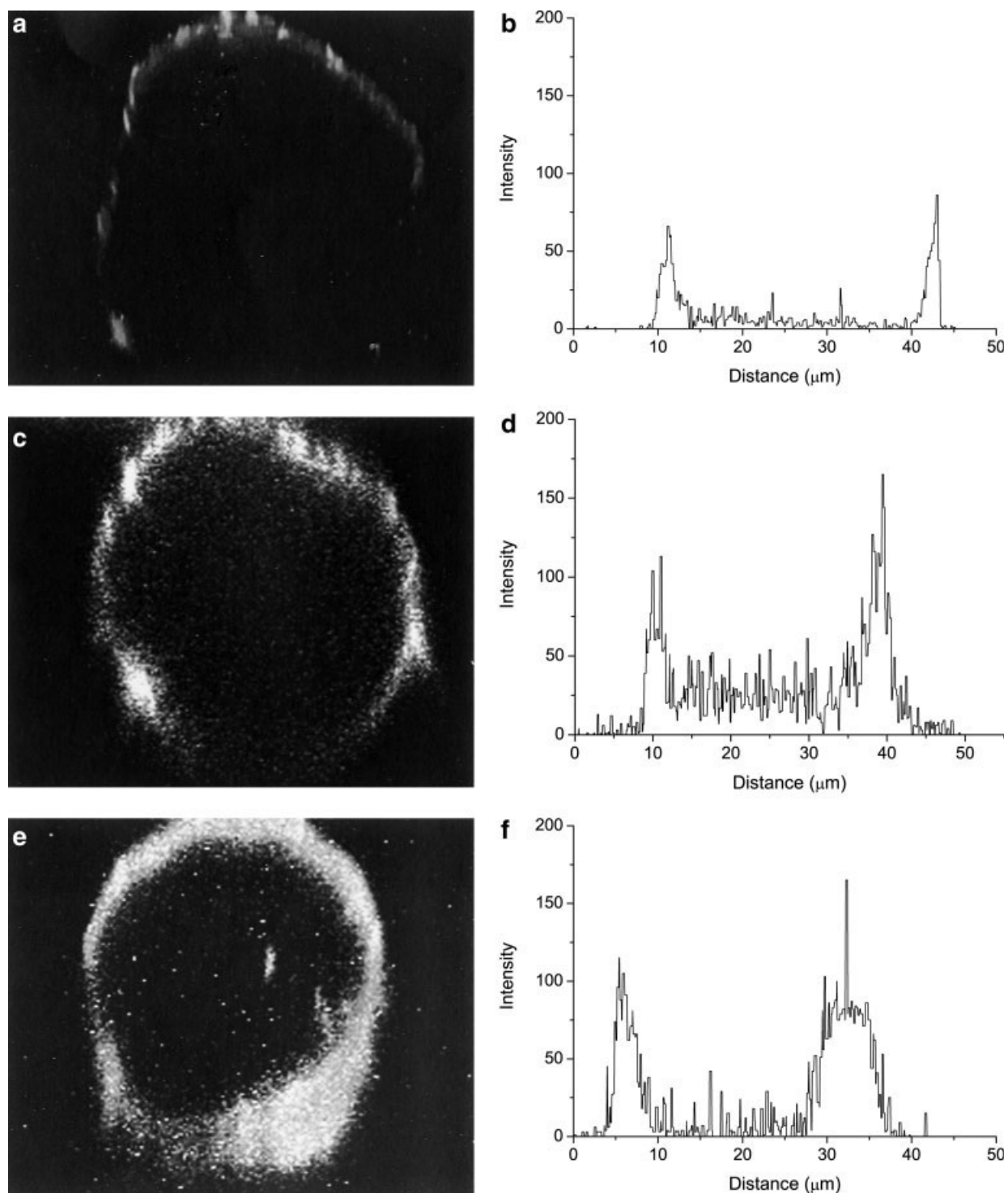


Figure 5 Images of the fiber cross-sections and the fluorescence intensity profiles across the fiber diameter: (a) cross-section and (b) intensity profile of the control fiber; (c) cross-section and (d) intensity profile of the fibers treated at 30°C 5 W; (e) cross-section and (f) intensity profile of the fibers treated at 30°C 10 W.

control specimen to a range of 66–77° for the treated specimens. All treated fibers were found to have statistically significantly lower contact angles in comparison with the control fibers. No significant differences were observed among the treated groups at the same temperature and different power input as

shown in Figure 4. Beyond the temperature of 60°C, an increase in temperature does not significantly alter the contact angle of the fiber. It is likely that the wettability changes of the treated fibers were resulted from the surface chemical modification as observed in XPS analysis.

TABLE IV
Interfacial Shear Strengths for UHMPE Fibers Untreated and Treated with Atmospheric Pressure Plasma Jet to Epoxy

Treatment	No. of specimens	IFSS (MPa)			
		Shear-lag model		Average over the embedded length	
		Mean	Standard deviation	Mean	Standard deviation
Control	18	5.26	1.57	3.07	1.47
30°C 5W	30	7.74	2.89	5.75	4.38
30°C 10W	23	9.63	3.15	5.56	2.47
60°C 5W	47	8.25	3.40	5.01	2.07
60°C 10W	46	9.09	3.75	5.31	2.43
100°C 5W	39	12.65	4.95	7.67	3.12
100°C 10W	32	8.63	2.90	4.64	1.62

Laser scanning confocal microscope

LSCM images of cross section of untreated and treated fibers were shown in Figure 5. As expected, the untreated fiber had almost no dyed region on the surface after being dyed for 30 min. This could result from the chemical inertness and low surface energy of UHMPE fibers. In contrast, the rings of treated fibers were obvious and continuous. The light intensity of treated fibers surface reached 160, twice as much as the untreated fibers (80). That could be attributed to the introduction of polar groups, creating the reactive sites at the fiber surface as determined by XPS analysis.

In addition, as shown in the intensity profiles, the dye molecules adsorbed by the plasma-treated fiber surfaces started to diffuse into the bulk while few dyed spots can be observed in the control fiber cross section, indicating the high concentration of fluorescence on the treated fiber surface resulted from the plasma treatment leading to a higher diffusion rate.

Adhesion measurements

The interfacial shear strength, τ_i , was calculated using the following equation, derived from the well-known shear-lag model:

$$\tau_i = \frac{nP_{\max} \coth(nL/r)}{2A}, \quad (1)$$

where P_{\max} is the peak load, A is the cross-sectional area of the fiber, L is the embedded length, r is the equivalent fiber radius calculated from the fiber cross-sectional area, and n is defined as:

$$n = \left[\frac{E_m}{E_f(1 + \nu_m) \ln(R/r)} \right]^{1/2}, \quad (2)$$

where E_m is Young's modulus of the matrix, ν_m is Poisson's ratio of the matrix, E_f is the tensile modu-

lus of the fiber, R is the radius of the epoxy beads, and r is the apparent radius of the fiber. R/r was about 8–12 for all the specimens. Typical load displacement curves of the microbond tests are similar to those presented in the literature⁴² and thus are not presented here since no additional information can be provided.

The results of the microbond test of the treated and the control fibers are shown in Table IV. From these data, it was found that the IFSS values for all plasma treated fibers increased by 57–140% comparable to the results obtained by Qiu et al.^{6,7} The plasma treatments roughened the fiber surface, changed the surface chemical composition, and decreased the contact angle significantly, leading to improved adhesion between the fibers and the resin.

There was no significant difference among all the treated groups except the highest value obtained at 100°C and 5 W power input, which was corresponding to the results of XPS analysis. The result of

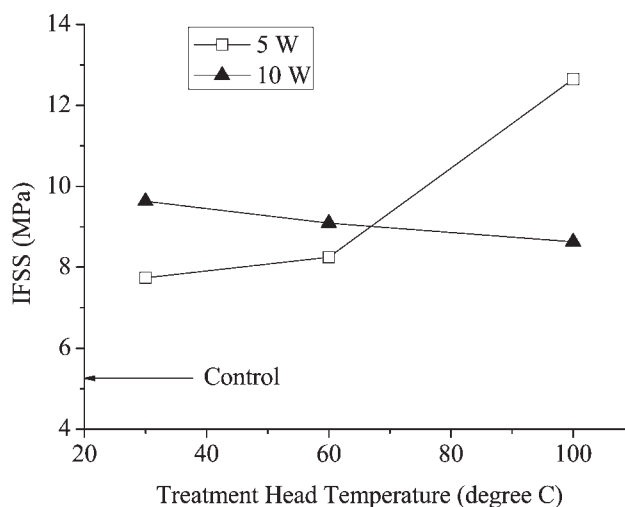


Figure 6 Change in interfacial shear strength for the control and the He plasma treated UHMPE fibers with different treatment conditions.

TABLE V
Single Fiber Tensile Strength of UHMPE Fibers
Untreated and Treated with Atmospheric Pressure
Plasma Jet

Treatment	No. of specimens	Tensile strength (GPa)	
		Mean	Standard deviation
Control	23	3.31	0.31
30°C 5W	25	3.08	0.23
30°C 10W	30	2.90	0.24
60°C 5W	26	2.91	0.24
60°C 10W	29	2.91	0.37
100°C 5W	29	2.98	0.55
100°C 10W	26	2.86	0.28

regression analysis showed the IFSS value strongly dependent on jet temperature. In contrast, the power input was of much less significance (see Fig. 6). It is interesting to note that the adhesion enhanced significantly within several seconds, which is much faster compared with most of low-pressure plasma treatments. It could be mainly due to the higher densities of active species in the APPJ.

Single fiber tensile strength

The tensile strength of UHMPE fiber either remained unchanged (30°C 5-W plasma treatments) or decreased by 10–13.6% after plasma treatment as shown in Table V. Similar results were reported by Muraoka et al.⁴³ who found 5-min oxygen plasma treatment resulted in a reduction on tensile strength of 15%. This could result from the ablation of the plasma, which ruptured the molecule chains of UHMPE fiber on the surface. For the unchanged group, it is not a surprise since the etching effect of the plasma was rather limited according to the SEM observation. After all, plasma surface treatments usually only affect a very thin surface layer of the fiber and should not influence bulk properties of the fiber significantly.

CONCLUSIONS

In this study, the effects of the treatment conditions of APPJ, namely plasma power input and treatment head temperature on the surface morphology and chemical composition, wettability, interfacial bond to epoxy, and the tensile strength of the plasma treated and the control UHMPE fibers were investigated. SEM analysis showed increased roughness of the fiber surfaces at submicrometer level for all treated fibers. Surface chemical analysis and LSCM analysis revealed an increased polar group number and increased affiliation of dyes to the fiber surface after plasma treatment at various conditions, which was considered an indication of significant surface modi-

fication by the plasma treatments. In general, a higher plasma treatment head temperature and a higher plasma power input give lower contact angles between the fiber and water. However, for IFSS, the combination of a lower plasma power input and a high treatment head temperature resulted in the best improvement.

The authors thank Ningbo Dacheng Company for providing UHMPE fibers. Special thanks to Dr. Xu Lin for allowing us to use LSCM in Shanghai Institute for Nutritional Sciences, Chinese Academy of Sciences. The authors also want to thank Mr. Chun Feng and Dr. Xu Guo for their help in the experiments and data analysis.

References

- Hild, D. N.; Schwartz, P. *J Mater Sci Mater Med* 1993, 4, 481.
- Hild, D. N.; Schwartz, P. *J Adhes Sci Technol* 1992, 6, 879.
- Hild, D. N.; Schwartz, P. *J Adhes Sci Technol* 1992, 6, 897.
- Moon, S. I.; Jang, J. *Compos Sci Technol* 1997, 57, 197.
- Luo, S.; Van Ooij, W. J. *J Adhes Sci Technol* 2002, 16, 1715.
- Qiu, Y.; Zhang, C.; Hwang, Y. J.; Bures, B. L.; Mccord, M. *J Adhes Sci Technol* 2002, 16, 99.
- Qiu, Y.; Hwang, Y. J.; Zhang, C.; Bures, B. L.; Mccord, M. *J Adhes Sci Technol* 2002, 16, 449.
- Moon, S. I.; Jang, J. *J Appl Polym Sci* 1998, 68, 1117.
- Andreopoulos, A. G.; Tarantili, P. A. *J Elastomers Plast* 1998, 30, 118.
- Zheng, Z.; Tang, X. Z.; Shi, M. W.; Zhou, G. T. *Polym Int* 2003, 52, 1833.
- Choi, D. M.; Park, C. K.; Cho, K.; Park, C. E. *Polymer* 1997, 38, 6243.
- Park, J. M.; Kim, D. S.; Kim, S. R. *J Colloid Interface Sci* 2003, 264, 431.
- Chung, Y. M.; Jung, M. J.; Han, J. G.; Lee, M. W.; Kim, Y. M. *Thin Solid Films* 2004, 447, 354.
- Yang, S.; Gupta, M. C. *Surf Coat Technol* 2004, 187, 172.
- Kim, B. K.; Kim, K. S.; Park, C. E.; Ryu, C. M. *J Adhes Sci Technol* 2002, 16, 509.
- Tsutsumi, K.; Ban, K.; Shibata, K.; Okazaki, S.; Kogoma, M. *J Adhes* 1996, 57, 45.
- Larrieu, J.; Held, B.; Clement, F.; Hiorns, R. C. *Eur Phys J Appl Phys* 2003, 22, 61.
- Noeske, M.; Degenhardt, J.; Strudthoff, S.; Lommatzsch, U. *Int J Adhes Adhes* 2004, 24, 171.
- Jeong, J. Y.; Babayan, S. E.; Schutze, A.; Tu, V. J.; Park, J.; Henins, I.; Selwyn, G. S.; Hicks, R. F. *J Vac Sci Technol A* 1999, 17, 2581.
- Lynch, J. B.; Spence, P. D.; Baker, D. E.; Postlethwaite, T. A. *J Appl Polym Sci* 1999, 71, 319.
- Hwang, Y. J.; Qiu, Y.; Zhang, C.; Jarrard, B.; Stedeford, R.; Tsai, J.; Park, Y. C.; Mccord, M. *J Adhes Sci Technol* 2003, 17, 847.
- Rahel, J.; Cernak, M.; Hudec, I.; Brablec, A.; Trunec, D.; Chodak, I. *Czech J Phys* 2000, 50, 445.
- Park, J.; Henins, I.; Herrmann, H. W.; Selwyn, G. S.; Jeong, J. Y.; Hicks, R. F.; Shim, D.; Chang, C. S. *Appl Phys Lett* 2000, 76, 288.
- Ferrero, F.; Tonin, C.; Peila, R.; Pollone, F. R. *Coloration Technol* 2004, 120, 30.
- Iriyama, Y.; Mochizuki, T.; Watanabe, M.; Utada, M. *J Photopolym Sci Technol* 2002, 15, 299.
- Sarmadi, A. M.; Kwon, Y. A. *Text Chem Colorist* 1993, 25, 33.

27. Park, S. J.; Jin, J. S. *J Colloid Interface Sci* 2001, 236, 155.
28. Ferrero, F. *Polym Test* 2003, 22, 571.
29. Song, Y.; Srinivasarao, M.; Tonelli, A.; Balik, C. M.; McGregor, R. *Macromolecules* 2000, 33, 4478.
30. Song, Y.; Srinivasarao, M.; Tonelli, A. *Macromol Symp* 1999, 148, 395.
31. Mcfarland, E. G.; Michielsen, S.; Carr, W. W. *Appl Spectrosc* 2001, 55, 481.
32. Lin, L.; Sosnowski, S.; Chaffey, C. E.; Balke, S. T.; Winnik, M. A. *Langmuir* 1994, 10, 2495.
33. Carroll, B. J. *J Colloid Interface Sci* 1976, 57, 488.
34. Carroll, B. J. *Text Res J* 1977, 47, 561.
35. Miller, B.; Gaur, U.; Hirt, D. E. *Compos Sci Technol* 1991, 42, 207.
36. Bhat, N. V.; Upadhyay, D. J.; Deshmukh, R. R.; Gupta, S. K. *J Phys Chem B* 2003, 107, 4550.
37. Cui, N. Y.; Brown, N. M. D. *Appl Surf Sci* 2002, 189, 31.
38. Jensen, C.; Zhang, C.; Qiu, Y. *Compos Interface* 2003, 10, 277.
39. Li, R.; Ye, L.; Mai, Y. *Compos A* 1997, 28, 73.
40. Kim, K. S.; Ryu, C. M.; Park, C. S.; Sur, G. S.; Park, C. E. *Polymer* 2003, 44, 6287.
41. Gao, S. L.; Zeng, Y. G. *J Appl Polym Sci* 1993, 47, 2093.
42. Hwang, Y. J.; Qiu, Y.; Zhang, C.; Jarrard, B.; Stedeford, R.; Tsai, J.; Park, Y. C.; McCord, M. *J Adhes Sci Technol* 2003, 17, 847.
43. Muraoka, Y.; Rich, M. J.; Drzal, L. T. *J Adhes Sci Technol* 2002, 16, 1669.