

Laser Scanning Confocal Microscope Characterization of Dye Diffusion in Nylon 6 Fibers Treated with Atmospheric Pressure Plasmas

Chunxia Wang,^{1,2,3} Lu Zhu,^{1,2} Yiping Qiu^{1,2}

¹State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Key Laboratory of Textile Science and Technology, Ministry of Education, China

²Department of Textile Materials Science, College of Textiles, Donghua University, Shanghai 201620, China

³College of Textiles and Clothing, Yancheng Institute of Technology, Yancheng, Jiangsu 224001, China

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ABSTRACT: The effect of atmospheric pressure plasma treatment on wettability and dyeability of nylon 6 fibers is investigated. The plasma treatments resulted in an average of 10°–20° decrease in the advancing contact angle and 20°–30° decrease in the receding contact angle. An increased dye diffusion rate of nylon 6 fibers was observed using laser scanning confocal microscope (LSCM). Scanning electron microscope confirmed that the fiber surfaces were roughened, and X-ray photoelectron spectroscopy showed that the polar groups on the fiber surfaces increased after the plasma treatments. As the plasma treatment time increased, a greater degree of etching was

achieved and more polar groups such as hydroxyl and carboxyl groups produced on the surfaces of the nylon 6 fibers, leading to a better wettability and thus a better dyeability of the fiber. This study proved that LSCM may be effectively used in detecting the change of dye diffusion rate in nylon fibers treated with plasmas and the mounting medium should have a close refractive index as the fiber to avoid distortion of the fiber cross section image. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1471–1478, 2008

Key words: plasma treatment; polyamide; wettability; dyeability; diffusion

INTRODUCTION

In the recent years, laser scanning confocal microscope (LSCM) has been used for the characterization of dye diffusion in fibers due to the fact that it has unique advantages over conventional cross-sectioning methods.^{1–4} LSCM is nondestructive and thus does not need to microtome single fibers. Furthermore, three-dimensional digital images of the fiber can be reconstructed and analyzed in various ways that would not be possible for a conventional cross-sectioning method. However, it has not been widely used in characterization of dyeing processes of textile fibers due to the following reasons. First, most of textile research laboratories do not have access to the instrument. Second, the types of dyes are limited to fluorescent dyes with certain wave lengths. Third, not enough information in published literature is available about this technique applied to textile

materials. For example, what the refractive index of the mounting medium should be to achieve good images of the fiber cross sections and how sensitive the technique would be for detecting the dye diffusion rate variation as a result of surface treatments.

Among all surface modification methods, plasma surface modification is a nonaqueous and environmentally friendly processing method, which does not involve large amount of water and chemicals. Therefore, low temperature plasma technology has been experimented for the surface modification of textiles such as improving wettability,⁵ water repellency,⁶ soil release,⁶ dyeing⁷ and printing properties,⁸ and depositing functional films on material surfaces.⁹ Most of the literatures published on improving dyeability and wettability are related to plasma treatment of polymer films^{10–15} and fabrics^{16–21} and relatively fewer of them deal with the surface modification of fibers by plasma treatment. Even less is known about the effect resulting from plasma treatment on dye diffusion in fibers. The improvement in dyeing is often described by the increment of *K/S* value and dyeing rate.^{22,23} When compared with these two macroscopical parameters, studies of dye diffusion and distribution in a single fiber cross section may shed more light on the mechanism of dyeability improvement after plasma treatment. Usually,

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

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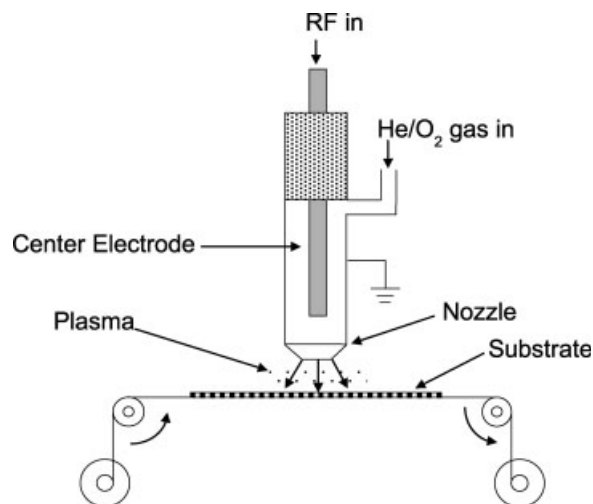


Figure 1 Schematic of the atmospheric pressure plasma jet treatment system.

the fibers are made into microtome sections and then observed by conventional optical microscope.²⁴ However, this method is destructive and cannot get the spatial distribution of dye molecules. In addition, cross-sectioning of single fibers is a rather tedious and time-consuming process.

This study investigated the effect of plasma jet treatment on the wettability of nylon 6 fibers measured by a dynamic contact angle analyzer and dye distribution in the fibers observed using LSCM for a better understanding of the mechanism of how plasma can improve dyeing properties of textile fibers and to illustrate how LSCM could be used to characterize the dyeability of polymeric fibers. Other surface characterization methods such as scanning electron microscopy, dynamic contact angle analysis,

and X-ray photoelectron spectroscopy are also used to show the surface chemical, physical, and morphological changes after the plasma treatments. Nylon 6 fiber was chosen as a model fiber because it is a typical textile fiber that can be dyed easily with the fluorescent dye used in LSCM. In addition, as a synthetic fiber, nylon 6 fiber has less variation in properties among different fibers or along the length of the fiber.

EXPERIMENTAL

Materials

Nylon 6 fibers were in a form of continuous filament yarns obtained from Yizheng Chemical Company (Jiangsu, China) with an average fiber diameter of 47 μm . The perpendicular and parallel refractive indices of the fiber are 1.519 and 1.582, respectively. Before the plasma treatment, the nylon fibers were washed in acetone for 30 min to remove the finishes and dried in a vacuum oven at room temperature. All fibers were then subjected to a heat-set treatment at 120°C to provide dimensional stability during the dyeing process. The fibers for plasma treatments were mounted on a wooden rectangular frame, which was later placed horizontally on the substrate conveying belt making a right angle to the plasma jet.

Plasma treatment

Plasma treatment of nylon 6 fibers was carried out in an atmospheric pressure plasma jet (APPJ) apparatus manufactured by Surfex Technologies (California). The substrate conveying belt system was fabricated to move the treated samples at a constant

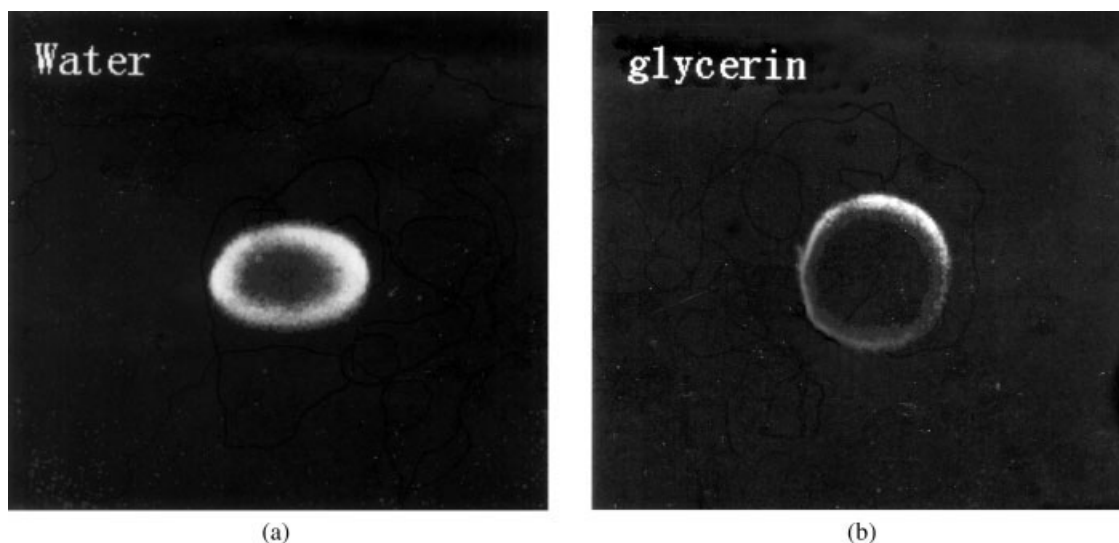


Figure 2 LSCM cross section images of nylon 6 fibers obtained using different mounting medium: water (a) and glycerin (b).

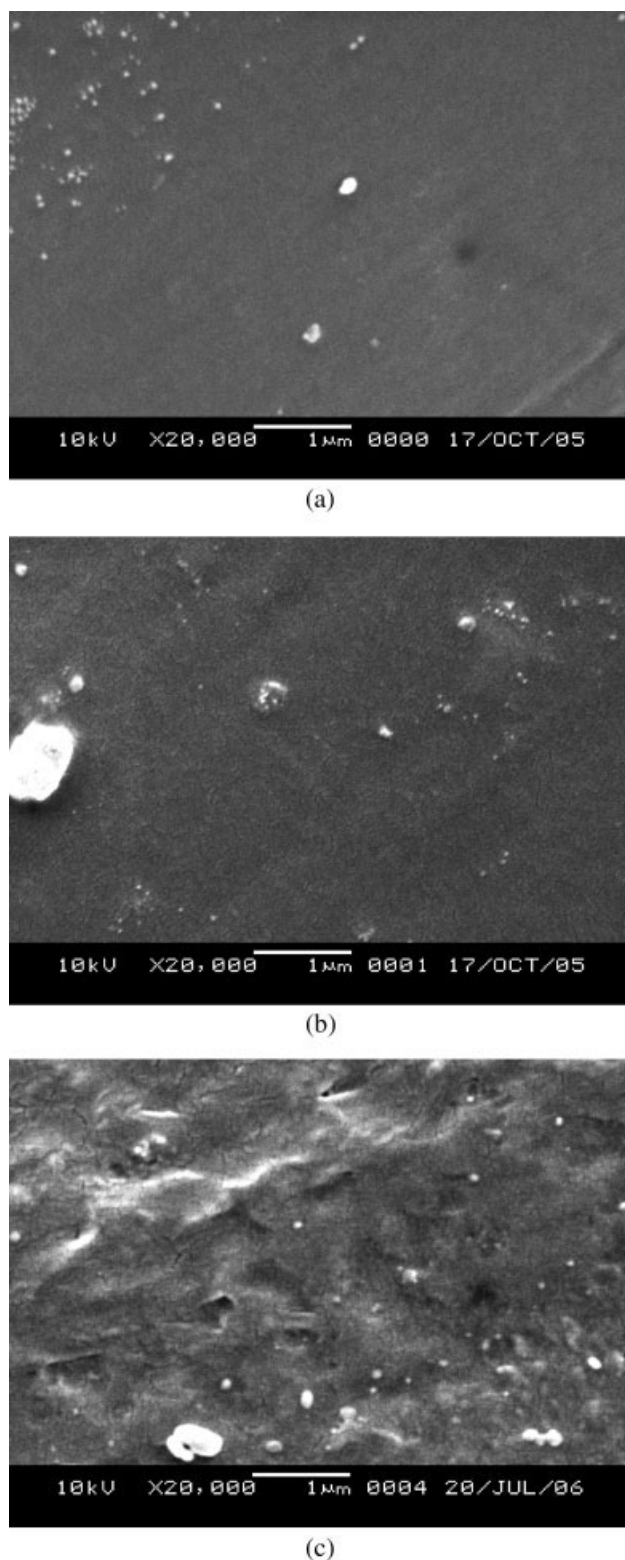


Figure 3 SEM photographs of the control and APPJ treated nylon 6 fibers: (a) control, (b) treated for 0.67 s, and (c) treated for 1.33 s.

speed. The schematic diagram of the plasma treatment system is shown in Figure 1. This device employs a capacitively coupled electrode design and

produces a stable discharge at atmospheric pressure with 13.56 MHz radio frequency power. The plasma jet system with a nozzle mounted above the conveying belt and covered an active area of $2 \times 10 \text{ mm}^2$. The fibers moved underneath the plasma jet at a speed of 3 mm/s. The carrier gas was helium with a flow rate of 10 L/min. The temperature of the treatment nozzle was set at 100°C , and the power was set at 10 W. Two groups of samples were respectively treated for one and two laps. The corresponding stationary treatment durations for the two samples were 0.67 and 1.33 s, respectively. The durations of the treatment were determined because in our previous studies, plasma treatment times of 0.67 and 1.33 s were found effective for improving wettability of aramid fibers²⁵ and ultrahigh molecular weight polyethylene fibers²⁶ although longer treatment time may result in better surface modification effect.

Wettability measurement

Immediately following the surface treatments, the effect of the plasma treatment on the wettability of the nylon fibers was evaluated by determining the advancing and receding contact angles of distilled water on fiber surfaces based on the Wilhelmy's plate technique.^{27–29} This was performed with Thermo Cahn DCA-322 dynamic contact angle analyzer. The advancing and receding contact angles, θ_a and θ_r , were calculated from the surface tension at the instant of immersion and withdrawal of a specimen from distilled water.

LSCM analysis

For LSCM analysis, the fibers were cut into about 2 cm and then dyed in a glass test tube with a fluorescent propidium iodide dye (a basic dye) solution with a concentration of 0.1 g/L at room temperature for about 30 min. The dyed fibers were then washed with distilled water and placed on a glass slide. In optical microscopy analysis of fibers, it is a common practice to select a mounting medium with a refractive index substantially different from that of the

TABLE I
Relative Chemical Composition and Atomic Ratios Determined by XPS for Nylon 6 Fibers Untreated and Treated with APPJ

Treatment	Chemical composition (atm %)			Atomic ratio		
	C1s	O1s	N1s	O/C	N/C	(O+N)/C
Control	73	21	6	0.29	0.09	0.38
Treated for 0.67s	68	24	8	0.35	0.12	0.47
Treated for 1.33s	66	25	9	0.37	0.14	0.51

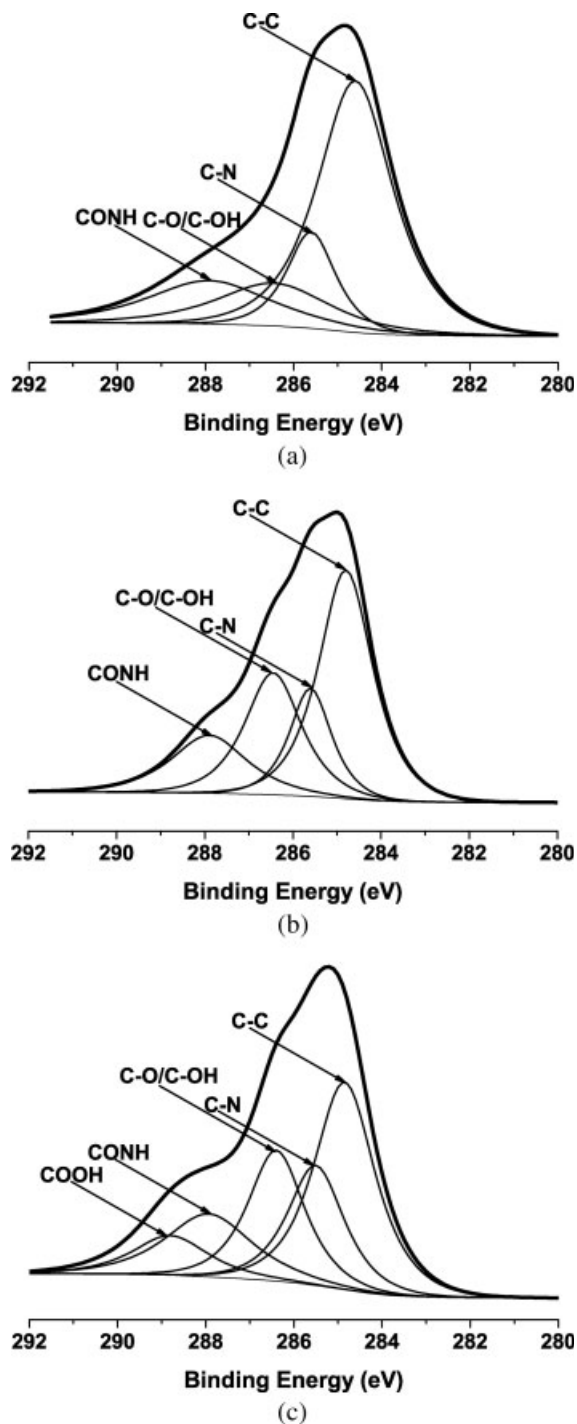


Figure 4 XPS C1s core-level spectra of the control and APPJ treated nylon 6 fibers: (a) control, (b) treated for 0.67 s, and (c) treated for 1.33 s.

fiber or the fiber will be hardly visible under the microscope. It is usually not a problem if the longitudinal views of the fibers are observed. For textile fibers, therefore, a commonly used mounting medium is water because it is easily available and has a refractive index of 1.33 different from all commercially available textile fibers. However, it was found

that the image of the fiber cross section was significantly distorted when water was used as the mounting medium. Figure 2 illustrates the images of the nylon fiber under LSCM using the two media. The image using water as medium was obviously substantially squashed. Therefore, to minimize the aberrations, it was realized that the refractive index of the mounting medium needed to be closely matched with that of the nylon fiber, which is about 1.56. Therefore, glycerin (refractive index of 1.48) was selected as the mounting medium, which gave a much better though still somewhat distorted image of the fiber.

The LSCM analysis was carried out using LSM 510 META microscope, which was equipped with a laser system of 543 nm wavelength. The images were obtained using xz scanning, thus providing an optical cross section of the fiber. In this process, the fiber was scanned from top to bottom by a laser beam and the intensity of the fluorescent light at each spot was recorded in a computer. Once the scanning was completed, the computer program reconstructed the 3D image of the fiber.

Analysis of surface morphology

The fiber surface morphology was examined using an SEM (model JSM-5600LV). The specimens were inspected at 20,000 \times magnification at 15 kV to see if there was any obvious change of fiber surface morphology caused by the plasma treatments. All of the samples were gold-coated prior to conducting the SEM observation.

Analysis of surface chemical composition

X-ray photoelectron spectroscopy 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), with the pass energy of 20 eV, and photo emitted electrons were collected at a take-off angle of 90°. 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 0.1 eV/step.

Single fiber tensile test

To determine if the plasma treatment could have any adverse effect on single fiber tensile strength, the tenacity of the fibers were tested. The linear densities of the fibers were measured by XD-1 Vibroscope (Shanghai Lipu Research Institute, Shanghai, China), and the single fiber tensile test was carried out on a XQ-1 Fiber Tensile Testing Machine (Shanghai Lipu Research Institute) at a gauge length

TABLE II
Results of Deconvolution of C1s Peaks for Nylon 6 Fibers Untreated and Treated with APPJ

Treatment	Relative area of different chemical bonds (%)				
	—C—C—	—C—N—	—C—O—/—C—OH	—O=C—NH	—O=C—OH
Control	55.98	13.95	14.28	15.79	0
Treated for 0.67s	43.95	16.14	24.43	15.48	0
Treated for 1.33s	35.91	19.23	20.95	15.46	8.45

of 20 mm and a cross-head speed of 10 mm/min under standard textile testing conditions of 20°C and 65% relative humidity.

Statistical analysis

One-way analysis of variance (ANOVA) and Tukey's pair-wise multiple comparison were employed to analyze test results of water contact angle and tensile strength.^{16,27} A *P*-value smaller than 0.05 was considered significant in all analyses.

RESULTS AND DISCUSSION

Morphological examination

The morphology changes on the nylon 6 fiber surfaces are shown in Figure 3. The plasma-treated fibers had a rougher surface than the control fibers. Longer treatment time resulted in a rougher fiber surface. The mechanism for plasma etching of fiber surfaces have been discussed in literature.^{7,30} This could increase the surface area and thus facilitating subsequent wetting and dyeing processes.

XPS analysis

Plasma treatment usually increases the hydrophilic polar groups on the fiber surface. XPS analysis results are shown in Tables I–III. Table I shows that the plasma treatment significantly changes surface chemical composition. It can be seen that plasma treatment increased O_{1s} and N_{1s} intensities. Moreover the contents of O_{1s} and N_{1s} increased with the increasing treatment time. After the plasma treatments the relative (O_{1s} + N_{1s})/C_{1s} core-level intensity increased by 21 and 34%. These changes can be explained by incorporating more oxygen and nitrogen atoms from the air onto the fiber surface during the plasma treatment process.

The XPS spectra for C_{1s} were deconvoluted for the specific functional groups as shown in Figure 4. The C—C bond with the binding energy of 285.0 eV was used as the reference for calibration. According to the literatures,^{11,12,18,31} polyamide fibers mainly have four carbon-containing peaks, i.e., C—C (285.0 eV), C—N (285.3 eV), C—O/C—OH (286.5), and CONH (288.0 eV), and two oxygen-containing peaks,

namely C—O/C—OH (531.6 eV), —C=O (533.3 eV). Tables II and III show the deconvolution analyses of C_{1s} and O_{1s} peaks elucidating the change of functional side groups. It can be seen from Table II that after plasma treatment, the amount of C—C group was decreased while —C—N— and —C—O—/—C—OH groups were increased. The amount of —C—OH was the largest for the fiber with treatment time of 0.67 s, while the fiber treated for 1.33 s showed more —COOH group. According to the results of O_{1s} peak deconvolution analysis in Table III, the amount of C—O—/—C—OH was increased significantly for the two plasma-treated samples compared with the control while the lower concentration of hydroxyl group and the higher concentration of carboxyl group were present in the fibers treated for 1.33 s, consistent with the results of C_{1s} peak deconvolution. The plasma treatments generated free radicals and other active species that reacted with the fiber surface to produce hydroxyl and carboxyl groups. The prolonged treatment time may lead to higher degree of oxidation reaction, which may turn more hydroxyl groups further into carboxyl groups for 1.33 s compared with the fibers treated for 0.67 s.³²

Effect of plasma treatment on wettability

Table IV shows the average advancing and receding contact angles for the control and the treated fibers with different treatment times. The values of the plasma-treated nylon 6 fibers ranged typically between 30° and 40° for the advancing contact angle and between 0° and 20° for the receding contact angle. The advancing and receding angles of the treated fibers decreased 10°–20° and 20°–30°, respectively. The

TABLE III
Results of Deconvolution of O1s Peaks for Nylon 6 Fibers Untreated and Treated with APPJ

Treatment	Relative Area of Different Chemical Bonds, %	
	C=O	C-O/C-OH
Control	83.18	16.82
Treated for 0.67s	71.18	28.82
Treated for 1.33s	76.59	23.41

TABLE IV
Advancing and receding water contact angles of nylon 6 fibers untreated and treated with APPJ

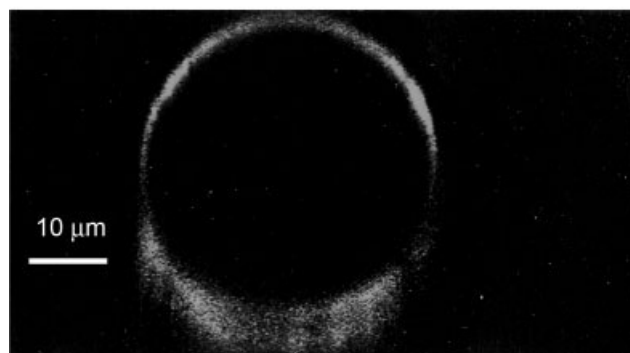
Treatment	Adv. contact angle θ_a (°)	Rec. contact angle θ_r (°)	Hysteresis $\theta_a - \theta_r$ (°)
Control	52.00 ^a ± 4.62	33.42 ^a	19
Treated for 0.67s	40.38 ^b ± 3.33	16.61 ^b	24
Treated for 1.33s	30.90 ^c ± 3.23	0 ^c	30

^a Means with different letters are statistically significantly different at $P < 0.05$.

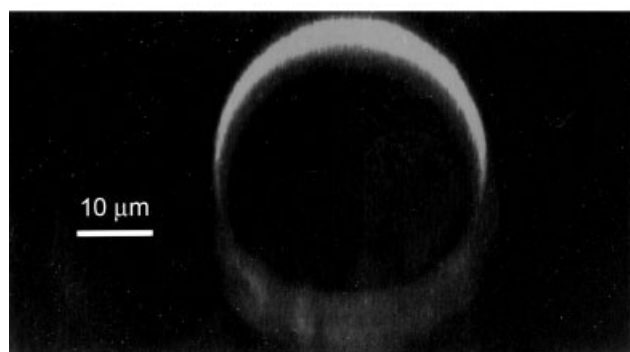
receding contact angles of treated fibers decreases more significantly than the advancing contact angles. In addition, longer treatment time resulted in a greater decrease of the advancing and receding con-



(a)

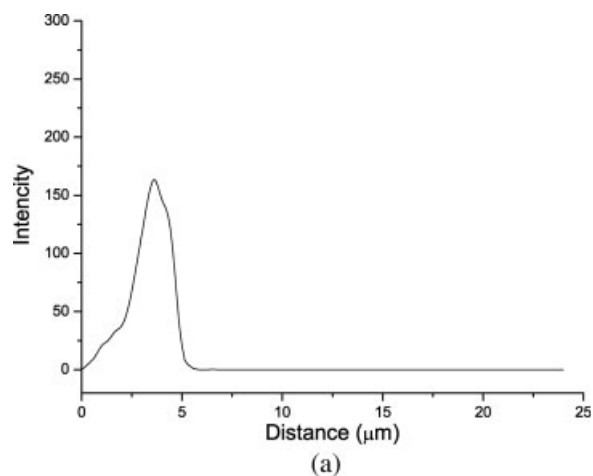


(b)

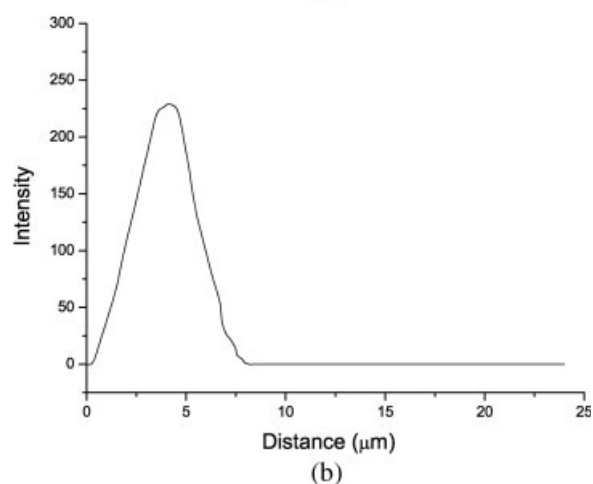


(c)

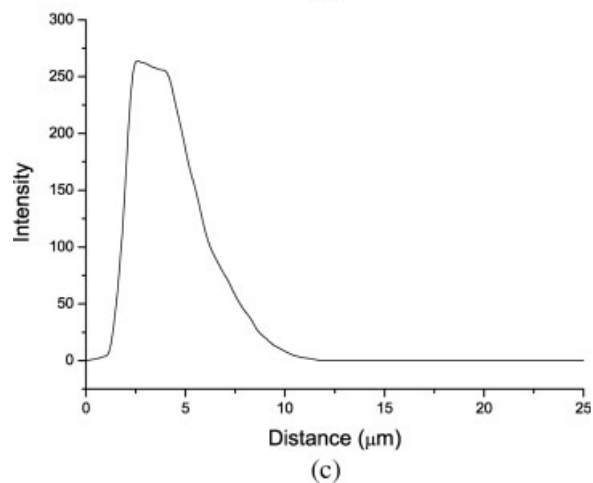
Figure 5 LSCM images of the cross section of (a) control, (b) treated for 0.67 s, and (c) treated for 1.33 s.



(a)



(b)



(c)

Figure 6 LSCM light intensity profile of (a) control, (b) treated for 0.67 s, and (c) treated for 1.33 s.

tact angles, similar to what has been reported in the literature.³³ The decrease of dynamic contact angles can be attributed to the increase of polar groups such as hydroxyl and carboxyl groups after the plasma treatments as shown in the XPS analyses.

The results in Table IV show that hysteresis ($\theta_a - \theta_r$) also increased with the increase of the treatment

TABLE V
Tensile Strengths of Nylon 6 Fibers Untreated and Treated with APPJ

Treatment	Number of specimen	Tensile strength (MPa)		P-value vs. control
		Mean	Standard deviation	
Control	34	497	18	—
Treated for 0.67 s	36	493	29	0.496
Treated for 1.33 s	36	489	22	0.093

time. In general, the contact angle hysteresis increases as surface roughness increases. SEM analysis of plasma-treated nylon 6 fibers indeed showed a significantly increased roughness on the nylon 6 fiber surface with treatment time of 1.33 s.

Effect of plasma treatment on dyeability

Figure 5 shows the dye spatial distribution in fiber cross sections. A significant difference was observed in diffusion profile between the control and the treated fibers. It can be seen that the fluorescent intensities of the treated fibers was much higher than that of the control. Moreover, the dyeing penetration depth of treated fibers was greater than that of control. In addition, the dyeing intensity and penetration depth increased as the treatment time increased, indicating a higher dye diffusion rate for longer treatment time.

The intensity profiles across the fiber cross sections are also shown in Figure 6. The width and the height of profile peaks for the treated fibers were both much bigger than those of the control, indicating more dye molecules diffuse deeper for the same dyeing duration for the plasma-treated samples.

It is generally accepted that the number of polar groups on fiber surface determines the onset of the dye penetration as the dye molecules diffuse from the solution to the fiber surface and then are adsorbed into the fiber bulk. This may be due to the formation of —OH and —COOH groups on the surface of the fiber after the plasma treatment that made the fiber surface even more negatively charged, facilitating the diffusion of the basic dye as suggested in literature.^{7,24}

Single fiber tensile strength

Table V shows the tensile strengths of the control and treated nylon 6 fibers. There was no statistically significant difference among the three groups since the plasma treatment lasted a very short time and could only affect the fiber surface similar to the results reported by others.^{29,34}

CONCLUSIONS

Nylon 6 fibers were treated with atmospheric pressure plasmas and the changes in dye diffusion for different treatment conditions were detected by LSCM. In LSCM measurement, it was found that a mounting medium with a refractive index as close to that of the fiber as possible should be used for the observation of polymeric fibers; the image could be distorted otherwise. Using LSCM, it was observed that the dye intensity and penetration depth increased greatly after the plasma treatment, indicating a greater dye diffusion rate for the treated fibers. Therefore, LSCM can indeed detect the change of dye diffusion in nylon fibers due to plasma treatment. The increased dye diffusion rates could be attributed to greater surface roughness, significantly increased surface oxygen and nitrogen contents, more hydroxyl and carboxyl groups on fiber surface, and decreased dynamic water contact angles after the plasma treatments. These effects were more profound for the longer treatment time. What presented in this study is just preliminary data and a systemic study with more dyeing experiments and more data from LSCM is underway at present time. It will be reported in our future publications.

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