Study on Wettability Improvement and Its Uniformity of Wool Fabric Treated by Atmospheric Pressure Plasma Jet

Chunxia Wang,[1,2] **Yiping Qiu**[2]

[1]*College of Textiles and Clothing, Yancheng Institute of Technology, Jiangsu, 224003 China*
[2]*College of Textiles, Donghua University, Shanghai, 201620 China*

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ABSTRACT: The influence of processing parameters on wettability improvement and its uniformity of wool fabric treated by atmospheric pressure plasma jet (APPJ) was explored. A woven wool fabric was treated by APPJ under various treatment conditions such as different treatment time, different oxygen flow rate, and different jet-to-substrate distance. The water absorption time of wool fabric was measured to determine wettability improvement. The diffusion photo of water droplet on wool fabric surface was taken by digital camera to reflect wettability uniformity. After APPJ treatment, SEM observation showed that the scales on the wool fiber surface directly facing plasma jet pores were destroyed than those on the other fiber surface. XPS analysis showed that the carbon concentration substantially decreased. The concentration of oxygen and nitrogen significantly increased and but the concentration of sulfur and silicon did not obviously changed. With the addition of oxygen gas, more polar groups such as hydroxyl and carboxyl produced on wool fiber surface. The water absorption time of wool fabric greatly reduced indicating wettability improvement. The diffusion of water droplet on wool fabric surface was also larger and more homogenous suggesting uniform plasma treatment. It was concluded that the wettability improvement and its uniformity of the treated wool fabric increased and then decreased with the increasing oxygen flow rate and jet-to-substrate distance, and increased with the increasing treatment time. Therefore to achieve reasonable wettability and its uniformity of the wool fabric treated by APPJ, plasma treatment conditions have to be carefully chosen. J Appl Polym Sci 123: 1000–1006, 2012

Key words: atmospheric pressure plasma jet; wool fabric; wettability; uniformity

INTRODUCTION

Wool is a kind of natural protein fiber with many excellent properties such as elasticity, abrasion resistance, and warmth retention. Wool is a typical hygroscopic textile material, whose moisture regain would be 12.1% and 26.6% at 65% relative humidity (RH) and 100% RH, respectively, however, with hydrophobic outmost layer on fiber surface.[1–3] Therefore, wool generally is hydrophobic in nature.[4–6] The existence of scales on wool fiber surface not only affects wettability and dyeability but also makes wool fabric felting shrinkage under hot/wet and mechanical actions.[7,8] Nowadays, the method for removing scales mainly includes chlorination[9–11] and enzyme treatment,[12–14] both of which could pollute environment severely due to a large amount of waste water and chemicals. With the increasing consciousness of environmental protection and economical restrictions imposed on textile industry, the wet procedure has to be replaced by environmentally favorable alternatives in wool treatment process.[15]

As a clean, dry, and environmental friendly process, plasma treatment is becoming popular and widely used in polymer surface modification without affecting bulk properties of substrate. Low temperature plasma technology has been experimented for the surface modification of textiles such as improving wettability, dyeability, adhesion, and so on in previous researches.[16–18] Most plasma treatments have been studied at low pressure, which involves a vacuum system and thus may not be a continuous process. Atmospheric pressure plasma treatment does not require a vacuum system and can be applied on-line for textiles. Two types of low temperature atmospheric pressure plasma are available, namely dielectric barrier discharge (DBD) and atmospheric pressure plasma jet (APPJ). APPJ is superior to DBD because it can generate uniform

Correspondence to: C. X. Wang (cxwang@mail.dhu.edu.cn).

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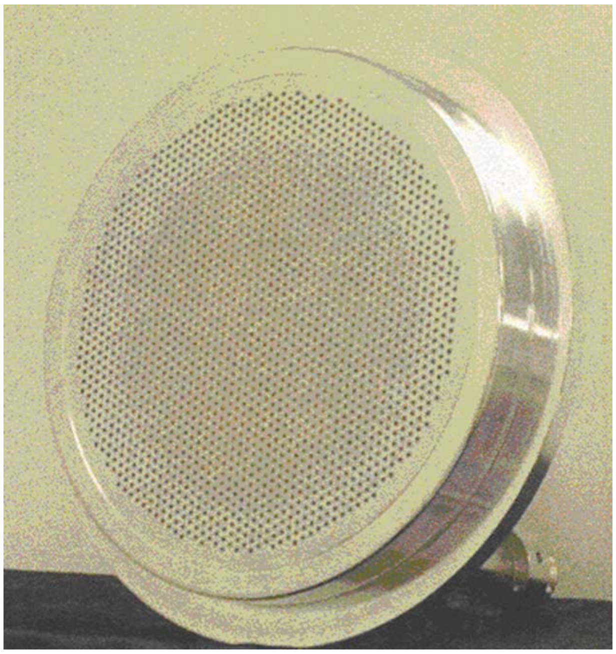

Figure 1 Plasma jet nozzle with many pores. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plasma and can also be applied to treat any shaped objects. However, APPJ is different from other plasmas. It works in an open system, in which plasma is produced between capacity coupled electrodes and then ejects from every pore in nozzle to form plasma jet. The substrate is not in complete and direct contact with active species in plasma jet. Therefore, property improvement and its uniformity of textiles treated by APPJ needs to be explored in detail. In this article, a woven wool fabric was treated under different treatment time, different oxygen flow rate, and different jet to substrate distance to see how these processing parameters influenced the wettability improvement and its uniformity. The wettability improvement was characterized as the change in water-absorption time of wool fabric. The diffusion photo of water droplet on wool fabric surface was taken to indicate the uniformity of wettability improvement. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were employed to determine surface changes in morphology and chemical composition. The optimal processing parameters for wettability improvement and its uniformity of wool fabric treated by APPJ were proposed.

TABLE I
Processing Parameters of APPJ Treatment

Parameter	Possible values
Output power (W)	***40***
Helium flow rate (L/min)	***20***
Treatment time (s)	***10***, 20, 30, 40
Oxygen flow rate (L/min)	0.1, ***0.2***, 0.3, 0.4
Jet-to-substrate distance (mm)	0.5, ***1***, 1.5, 2

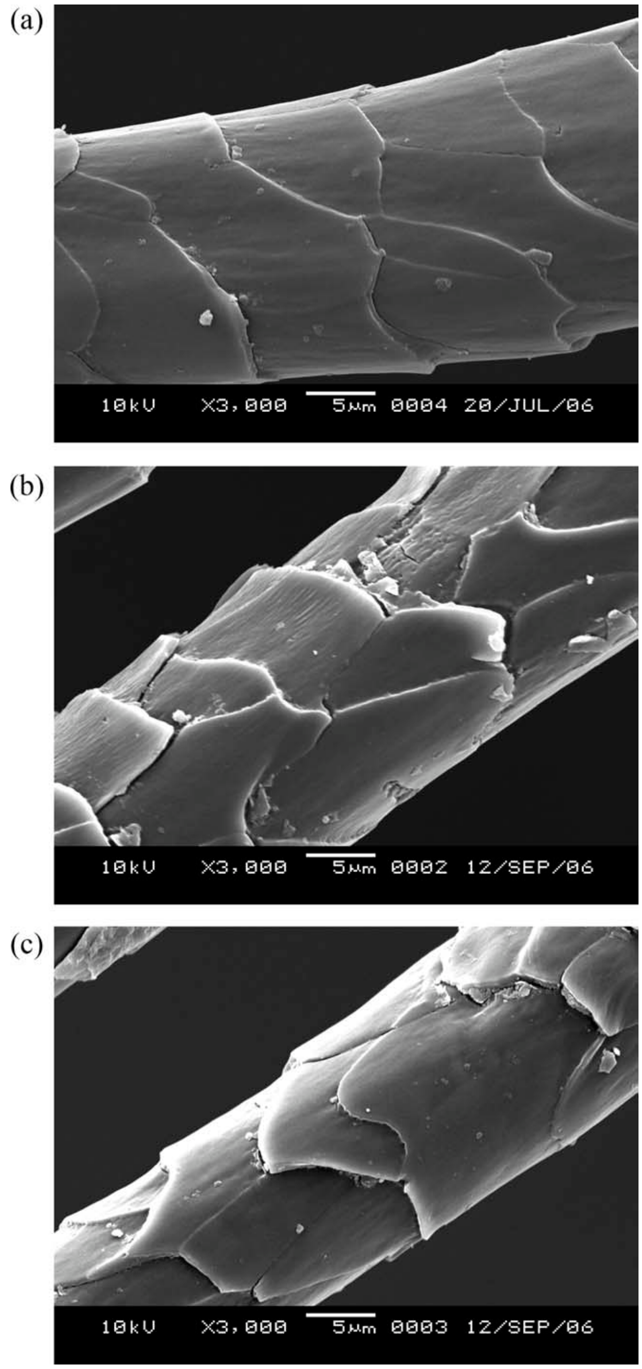

Figure 2 SEM micrographs of wool fiber surface before and after APPJ treatment: (a) control, (b) directly facing plasma jet pore, and (c) not directly facing plasma jet pore.

EXPERIMENTAL

Materials

The fabric specimen used in this study was a plain weave wool fabric (14.7 tex × 2 ply warp and 40 tex × 2 ply weft; 280 g/m^2). The thickness of the fabric

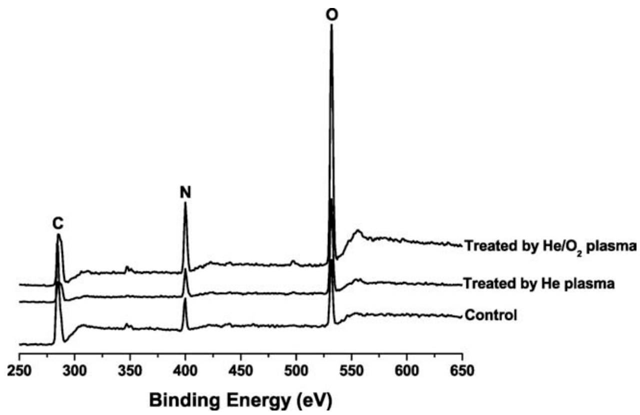

Figure 3 XPS survey scan of wool fiber surface before and after APPJ treatement.

was about 0.635 mm. Before plasma treatment, the wool fabrics were scoured with acetone for 30 min to clean the fabric and then dried in a vacuum oven at room temperature for 12 h. Then the cleaned fabrics were cut into the size of 30 mm × 30 mm and mounted on a rectangular wooden frame.

Plasma treatments

Plasma treatment of wool fabric was carried out on an atmospheric pressure plasma jet apparatus manufactured by Surfix Technologies (CA). This device employs a capacitively coupled electrode design and produces a stable discharge at atmospheric pressure with 13.56 MHz radio frequency. A round nozzle with an active area of 3.14 × 2.5 cm^2 and many pores (as shown in Fig. 1) was mounted vertically above the substrate. Helium and oxygen were used as carrier and reactive gases. The processing parameters are listed in Table I. When one parameter changed, the other parameters were held constant as shown in boldface and italic font in Table I.

Wettability and its uniformity measurements

The wettability of wool fabric was measured according to the BS4554:1970. A microliter syringe was used to place a distilled water droplet of 2 μL on

TABLE II
Relative Chemical Composition and Atomic Ratios Determined by XPS for Wool Fabric Surface Before and After APPJ Treatment

	Chemical composition (%)					Atomic ratio
Sample	C	O	N	S	Si	(O + N)/C
Control	69.1	17.2	10.0	2.9	0.8	0.40
Treated by He plasma	41.6	38.1	17.0	2.8	0.5	1.32
Treated by He/O_2plasma	37.6	42.0	17.4	2.3	0.7	1.58

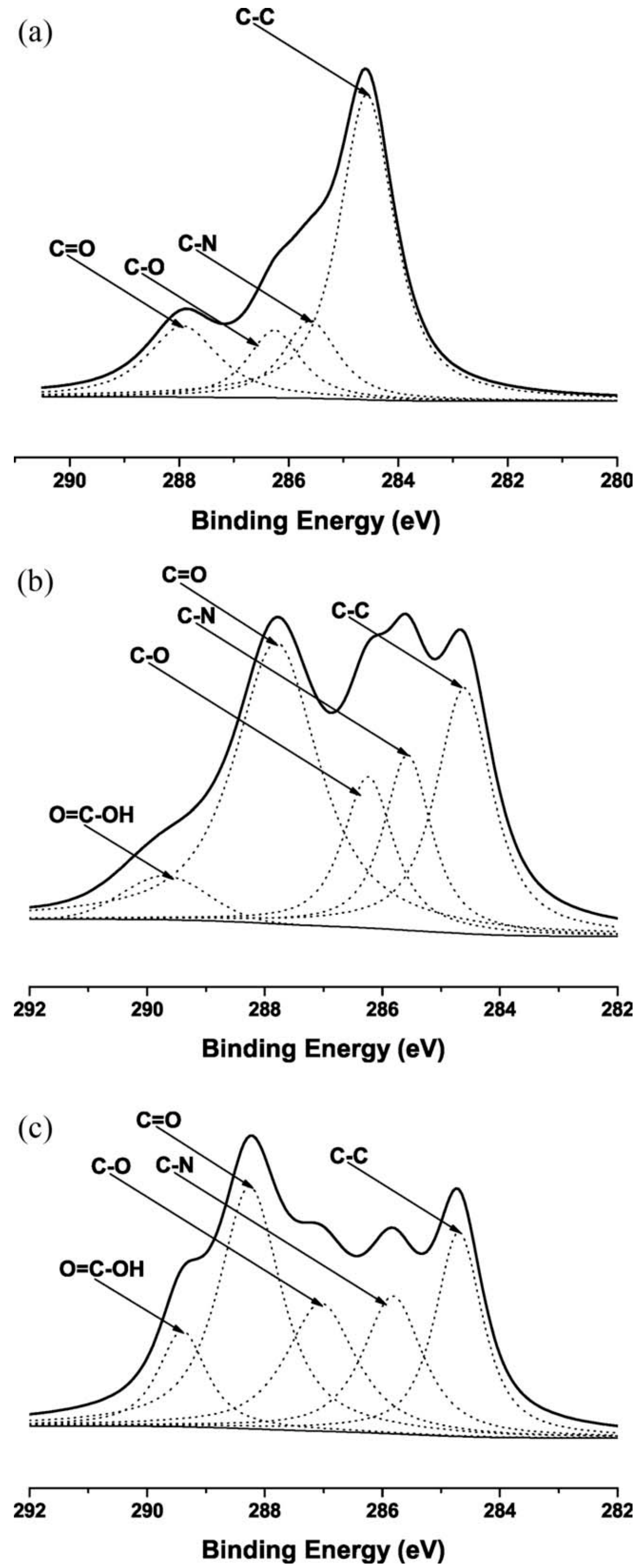

Figure 4 Deconvolution of XPS core level C1s spectra of wool fiber surface before and after APPJ treatment: (a) control, (b) treated by helium APPJ, and (c) treated by helium/oxygen APPJ.

fabric surface. The time for water droplet to be completely absorbed into fabric was taken as water-absorption time.[18,19] Five measurements were taken

TABLE III
Results of the Deconvolution of C1s Peaks for Wool Fabric Surface Before and After APPJ Treatment

	Relative area of different chemical bonds (%)				
Sample	-C-C-	-C-N-	-C-O-	-O=C-	-O=C-OH
Control	56.6	14.3	12.0	17.1	0
Treated by He plasma	25.7	15.4	14.1	39.9	4.9
Treated by He/O_2 plasma	20.9	17.7	19.1	32.4	9.9

for each sample. The diffusion photo of water droplet on fabric surface was taken using an Olympus CH-2 microscope equipped with a Panasonic WV-GP410/A digital photomicrography system.[20]

SEM observation

The surface morphology of wool fiber was examined using a SEM (model JSM-5600LV). The image magnification was set at 3000×. The fibers were coated with gold before conducting SEM observation.

XPS measurement

The surface chemical composition of wool fiber was analyzed by XPS measurement on Thermo MICROLAB MKII system equipped with a Mg Ka (1253.6 eV) X-ray source. The measurement was carried out under UHV conditions (10^{-7} to 10^{-8} Pa). The power was set at 300 W and the spectra were taken at the take-off angle of 45°.

RESULTS AND DISCUSSION

Surface morphology analysis

The SEM images of wool fiber surface before and after APPJ treatment are shown in Figure 2. As we known, the surface of untreated wool fiber is covered with compact and intact scales, in which the presence of a microporous hydrophobic layer called epicuticle makes wool fiber surface difficult to get wet. However, it could be seen that the scales were broken, and some cracks appeared on the surface of the treated wool fiber. This was attributed to plasma etching effect caused by the bombardment of active species from plasma jet with fiber surface. In addition, the scales on the fiber surface directly facing plasma jet pore were more severely damaged than those on the other fiber surface due to more active species accumulating on the fiber surface underneath plasma jet pore. Meanwhile, the wool fiber surface became rougher because of plasma etching effect. All these changes contributed to wettability improvement of the wool fabric treated by APPJ.[19,21]

Surface chemical composition analysis

XPS survey scan and chemical composition of wool fiber surface before and after APPJ treatment is shown in Figure 3 and Table II. The surface composition of

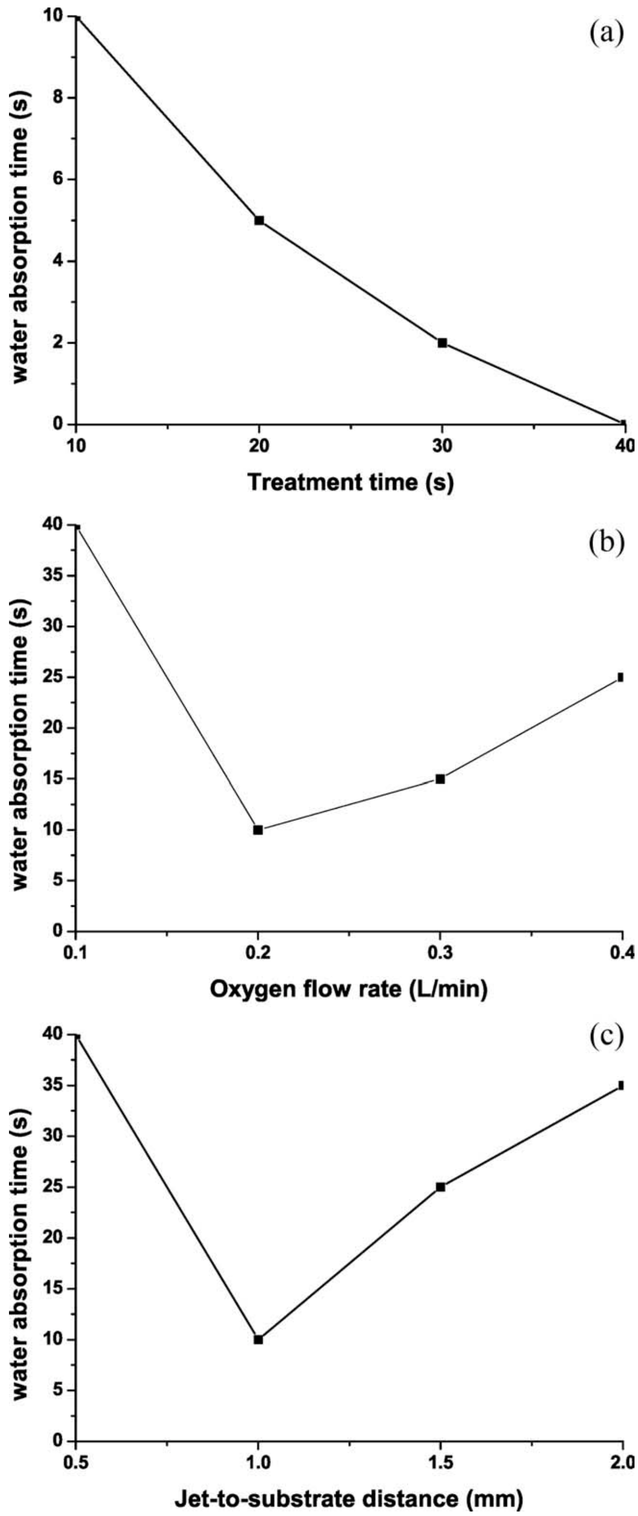

Figure 5 Influence of processing parameters on water-absorption time for the treated wool fabric: (a) oxygen flow rate, (b) jet-to-substrate distance, and (c) treatment time.

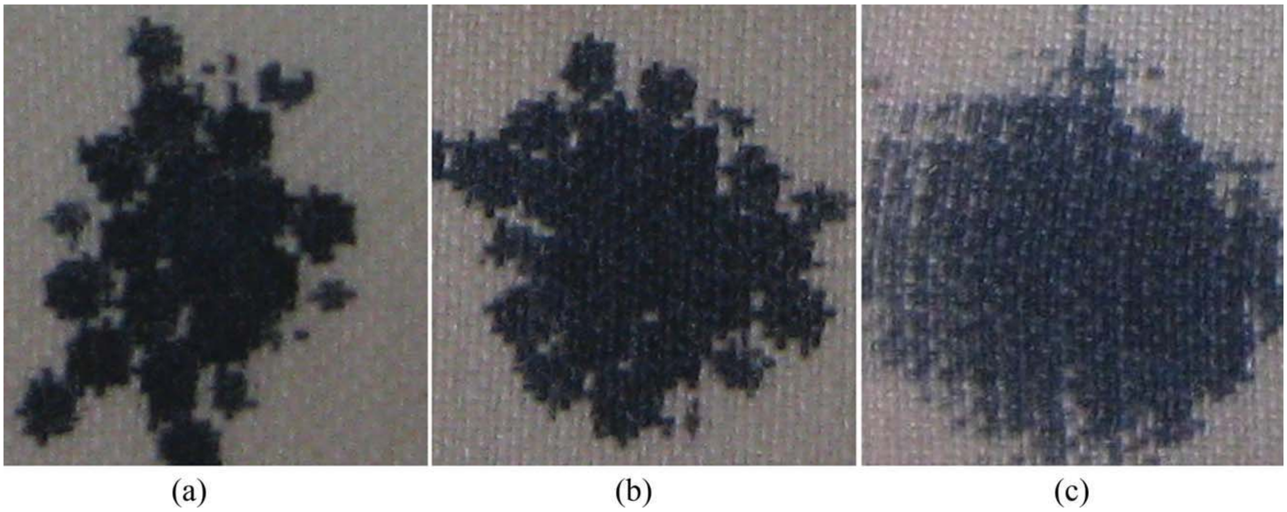

Figure 6 Influence of treatment time on diffusion of water droplet on the treated wool fabric surface: (a) 20 s, (b) 30 s, and (c) 40 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

untreated wool fiber is similar to that reported in literatures.[20,22,23] The outermost part of epicuticle membrane is covered with fatty acid monolayer containing high concentration of carbon. Beneath fatty acid monolayer locates protein layer containing some nitrogen and sulfur forming disulphide bonds. The detected sulfur is also from thioester linkage between fatty acid and protein layer. Most oxygen is attributed to amide bond and other hydrophilic groups and some oxygen is related to the impurities of silicon from organic silicon-softening agent applied during previous finishing process.

It could be seen that there was a significant decrease in carbon concentration and a progressive increase in oxygen and nitrogen concentration. The decreased carbon and the increased oxygen could be the oxidation of hydrocarbon chains from fatty acid monolayer. As reported by Molina et al.[23] that no oxidized functionalities on N1s peak discarded the possibility of the introduction of nitrogen species on the external layers of wool fiber surface. Therefore, the increased nitrogen might be explained by that the fatty acid monolayer was removed by plasma etching and the underlying protein layer was visible on wool fiber surface. The sulfur and silicon concentration did not change after different plasma treatment as found in previous studies.[7,15,23] With the addition of oxygen gas, the changes in carbon and oxygen concentration were more significant, which showed that active species of oxygen molecules facilitated more progressive oxidation of hydrocarbon chains, however, the change in nitrogen concentration was not significant, which could mean that oxygen gas did not affect plasma etching and thus no more protein layer was exposed on wool fiber surface.

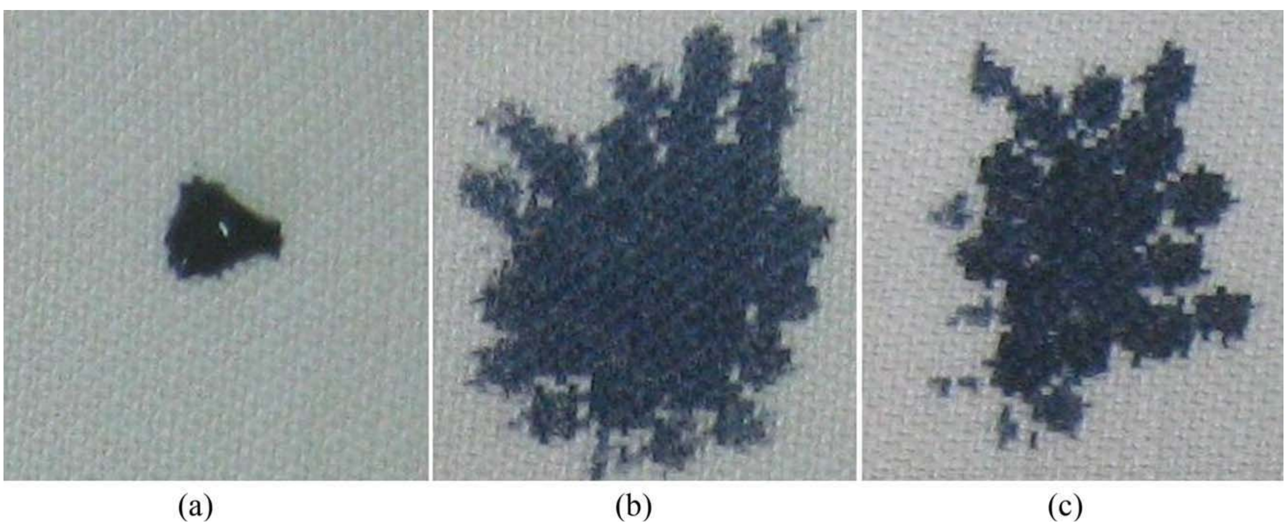

Figure 7 Influence of oxygen flow rate on diffusion of water droplet on the treated wool fabric surface: (a) 0 L/min, (b) 0.2 L/min, and (c) 0.3 L/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

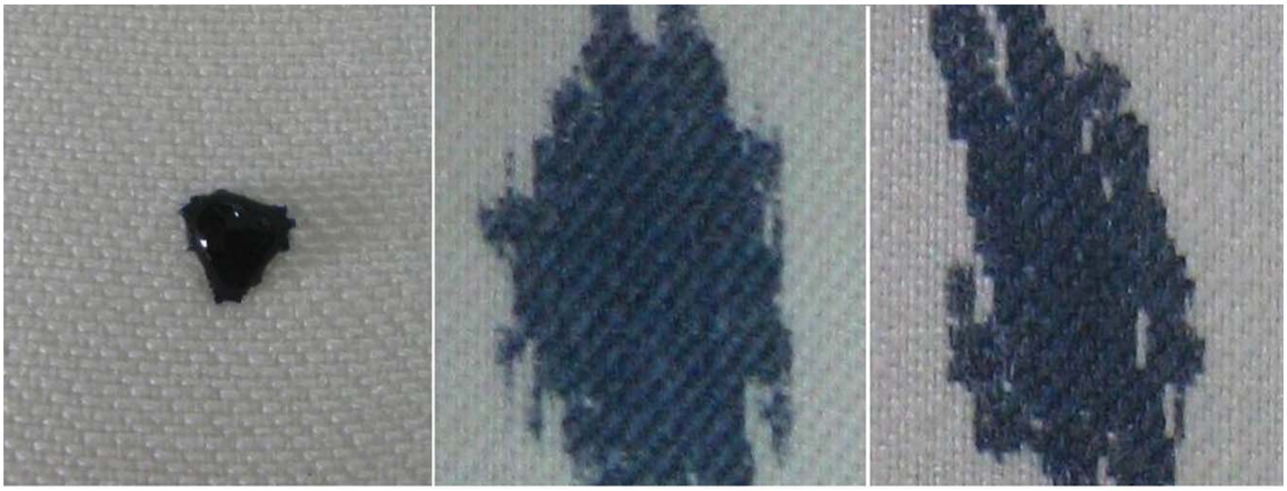

Figure 8 Influence of jet-to-substrate distance on diffusion of water droplet on the treated wool fabric surface: (a) 0.5 mm, (b) 1 mm, and (c) 1.5 mm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For further analysis, the C1s spectrum was deconvolved with XPSPEAK software as shown in Figure 4 and the detailed data are shown in Table III. The deconvolution analysis results of C1s peak could elucidate the changes in functional side groups before and after plasma treatment. Based on literatures,[7,20,22,23] the carbon-containing groups on wool fiber surface could be attributed to C—C (284.6 eV), C—N (285.6 eV), C—O (286.5 eV), and C=O (288.0 eV). After plasma treatment, there appeared a new peak at 289.4 eV corresponding to O—C—OH. The concentration of aliphatic carbon and carbon–oxygen groups drastically decreased and increased, respectively, which fundamentally contributed to wettability improvement of the wool fabric treated by APPJ.[24,25] The more oxygen-containing functionalities such as hydroxyl and carboxy were introduced on wool fiber surface with the addition of oxygen gas. It could be explain by the oxidation of aliphatic carbon (C—C) into hydroxyl-like groups (C—O) and the oxidation of carbonyl (O=C) into carboxyl (O=C—OH) due to the more active molecules and excited species in He/O_2 plasma and the H_2O presence both in the plasma and in the atmosphere.[26–28] This hypothesis was supported by the fact that the plasma oxidation of wool fiber surface would follow the process: C—C→C—O→C=O→O—C=O.[29]

Wettability improvement and uniformity

Figure 5 shows the changes in water absorption time of the treated wool fabric as functions of processing parameters. Figures 6 to 8 show the diffusion of water droplet on the wool fabric surface treated by AAPJ under different processing parameters. With the increasing treatment time, the water absorption time of wool fabric decreased and the uniformity of water droplet on wool fabric surface increased, indicating the better wettability and its uniformity with the longer treatment time. When the wool fabric was treated for about 40 s, the water droplet on wool fabric surface immediately and uniformly diffused. As the increase of treatment time, the more active species from plasma jet accumulating on wool fabric surface could react with the larger area including the surface not directly facing plasma jet pore.[29]

With the increasing oxygen flow rate and jet-to-substrate distance, the wettability and its uniformity of wool fabric increased and then decreased, indicating the better wettability and its uniformity with appropriate oxygen flow rate and jet-to-substrate distance. When oxygen flow rate and jet-to-substrate distance were set as 0.2 L/min and 1 mm, the water droplet on wool fabric surface immediately and uniformly diffused. When a small amount of oxygen gas was added to helium, the number and activity of active species increased, which facilitated plasma treatment effects. However, the addition of excessive oxygen gas increased breakage voltage resulting in unstable discharge due to its quenching effect, which weakened plasma treatment effects.[30–32] When the jet-to-substrate distance was too small, most active species from plasma jet were almost blocked by fabric surface, and the plasma jet could only be bounced off fabric surface and flew out in a more parallel to fabric surface direction, which greatly reduced plasma treatment effects. When the jet-to-substrate distance was too large, the velocity and activity of active species in plasma jet greatly reduced when reaching fabric surface and thus they would have no enough energy to modify fabric surface.[33]

CONCLUSIONS

After a woven wool fabric was treated by APPJ under different treatment time, different oxygen flow rate, and different jet-to-substrate distance, the scales on wool fiber surface were damaged to a different degree and the number of polar groups greatly increased. The wettability improvement and its uniformity of the treated wool fabric were closely related to treatment time, oxygen flow rate, and jet-to-substrate distance. The longer treatment time and the appropriate oxygen flow rate and jet-to-distance could help wettability improvement and its uniformity of the treated wool fabric. Therefore, adequate plasma processing parameters have to be carefully selected. The best treatment results for wettability improvement and its uniformity of the treated wool fabric were obtained when helium and oxygen flow rate, jet-to-substrate distance, and treatment time were set as 20 L/min, 0.2 L/min (O_2/He:0.01), 1 mm and more than 40 s, respectively.

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