Influence of Absorbed Moisture on Antifelting Property of Wool Treated with Atmospheric Pressure Plasma

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Received 30 November 2008; accepted 2 March 2009
DOI 10.1002/app.30429

ABSTRACT: To determine the effect of moisture regain of wool on atmospheric pressure plasma treatment results, wool fibers and fabrics conditioned in 100% relative humidity (RH) and 65% RH were treated by an atmospheric pressure plasma jet with pure helium and helium/oxygen mixed gas, respectively. Scanning electron microscope (SEM) indicated that scales of wool fiber were smoothened for fibers conditioned in the 100% RH. X-ray photoelectron spectroscopy (XPS) showed that carbon content decreased substantially after the plasma treatment. Surface chemical composition of 100% RH conditioned groups changed more significantly than the 65% RH conditioned groups. Water contact angle decreased significantly after the plasma treatments. In shrinkage test, plasma-treated wool fabrics preconditioned in 100% RH showed the lowest shrinkage ratios of 5% and 6%, below 8% is required for machine-washable wool fabrics according to ISO standard. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3687–3692, 2009

Key words: wool; atmospheric pressure plasma; relative humidity; SEM; XPS; contact angle; antifelting

INTRODUCTION

The presence of scales on wool fiber surface makes wool fabric felting and thus shrinking upon laundry because of their differential friction effect (DFE). Traditional methods for shrink resistance of wool fabric include chlorination and polymer deposition (Hercosett treatment), both of which could pollute the environment severely by producing effluent containing high level of adsorbable organic halogens (AOX).[1] New techniques such as enzyme treatment,[2–4] which could modify scales without damaging cortex of wool, and chitosan treatment,[5,6] which could cover scales to reduce DFE, have been developed to replace chlorination method. Both of the methods prevent producing effluent with AOX. However, as wet processes, these techniques still have to consume large amount of water. Moreover, most of the new methods could not achieve satisfactory antifelting results without combining with other techniques.[7] As the environmental concern rises, plasma treatment, as a nonaqueous technique, is becoming a favorable alternative to wet-finishing process in textile industry.

Plasma treatments have been used to improve adhesion, wettability, dyeability, and some other properties of textiles.[8–11] Depth of plasma treatment is confined to the surface while the bulk properties of the substrate are not affected.[12] Substantial attention has been paid in using plasma treatments to improve dyeing and shrink-resistant properties of wool.[12–14] However, treatment results have been unsatisfactory even with prolonged plasma treatments without the assistance of other techniques.[15,16]

Wool is a typical hygroscopic textile material that could absorb 12.1% and 26.6% moisture of its dry mass at 65% relative humidity (RH) and 100% RH, respectively, however, with hydrophobic outmost layer on fiber surface.[17–19] Difference in wettability between the core part (cortical cells) and the sheath part (cuticle) of wool leads to differential deformation upon absorbing water.[20] Larger angles between the scales and the wool fiber axis facilitate interaction of many agents with wool surface. According to our previous study on the influence of moisture on the effect of atmospheric pressure plasma treatment,

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Contract grant sponsor: National High Technology Research and Development Program of China; contract grant number: 2007AA03Z101.

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

Contract grant sponsor: Program of Introducing Talents of Discipline to Universities; contract grant number: B07024.

Contract grant sponsor: National College Student Innovative Research Program, Donghua University Undergraduate Education Reform Project.

Journal of Applied Polymer Science, Vol. 113, 3687–3692 (2009)

absorbed water plays an important role in the atmospheric pressure plasma treatment of hygroscopic materials.[21–24] In particular, influence of moisture content on plasma etching effect has been investigated for polyamide fibers with different amide group content and backbone structures, such as nylon, aramid, and wool.[23] It was observed that plasma etching effect was most significant for polyamide fibers conditioned in 100% RH environment. Scales of wool fibers conditioned in 100% RH could be thoroughly removed, whereas in low-pressure plasma treatment on wool, prolonged plasma exposure could result in obvious damage of scales instead of smoothening them.[16] If wool fibers can be smoothened by plasma treatment only, this technique alone should be able to make wool fabric felting free or resistant to shrinking upon laundry. However, no one has reported how moisture regain of wool fiber when treated with plasmas may affect antifelting properties of the plasma-treated wool fabrics. In this study, we systematically investigated the effect of environment RH on the etching of wool fibers in plasma treatments and the subsequent antifelting properties of wool fabrics treated at the same conditions. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), water contact angle, and shrink resistance test were employed to determine the change of the surface morphology, surface chemical composition, surface wettability, and fabric shrink resistance of wool because of the plasma treatments in two different RH conditions.

EXPERIMENTAL

Materials

A weft-knitted (single jersey) pure wool fabric was produced with 64s commercially available wool yarns. The same wool fibers (provided by Linglong Textile Company, Jiaxing, Zhejiang Province, China) were also used in the experiment for single fiber tests. All samples were scoured twice in acetone for 30 min to eliminate potential contamination and vacuum dried for 12 h at room temperature. The cleaned fabrics were cut into 10 cm × 10 cm pieces for shrinkage test. Before plasma treatment, all the samples were conditioned for 12 h at 65% and 100% RH.

Plasma treatments

An atmospheric pressure plasma jet (APPJ) Atomflo^{TM}-R (Surfx Technologies, CA) was used for the treatment of wool fabrics and fibers. A capacitively coupled electrode design is employed in the device to produce stable discharge with 13.56 MHz radio frequency power at atmospheric pressure. The power was set at 40 W. Two types of gases, pure helium at a flow rate of 20 L/min and helium at a flow rate of 20 L/min with oxygen at a flow rate of 0.2 L/min were employed in the APPJ treatment. The samples were placed on a conveying belt moving at a speed of 3.6 mm/s, and the distance between sample and nozzle was 2–3 mm. The diameter of active area of the nozzle was 20 mm. The temperature on the surface of the sample was about 60°C. Each sample was treated for two laps. To maintain the moisture in the wool fibers, plasma treatment was carried out in a sealed chamber with an adjustable RH.

Surface morphology analysis

SEM (JSM-5600LV Model, Japan) was employed to analyze the surface of the untreated and the treated samples. The magnification of the image was set at 5000×. The fibers were coated with gold before testing.

Surface chemical composition analysis

XPS spectra of the fiber surface were obtained at a MICROLAB MKII X-ray photoelectron spectrometer with a Mg Kα (1253.6 eV) X-ray source. The pass energy was 20 eV and take-off angle was 45°. The inspection was carried out under a vacuum condition of 10^{-7} and 10^{-8} Pa. The original data were subjected to deconvolution analysis using XPSPEAK software. The deconvolution analysis for C1s peaks in the XPS spectra was performed using C—C bond as a reference subpeak at 285 eV and all other subpeaks, namely —C—O (286.8 eV) C=O (288.4 eV) and COOR (289.6eV) were shifted accordingly.

Contact angle test

The contact angle test was carried out on an OCA40 Micro system (Dataphysics, Germany), which could record the whole absorption process. A droplet of distilled water was placed on a single fiber fixed on the holder. Initial contact angle of the wool fiber and the absorption time were determined.

Shrink resistance measurement

The shrink resistance test was performed following ISO 6330. A knitted wool fabric was considered as "machine washable" while the area shrinkage ratio was below 8% for knitted wool after three laundry cycles.

Before shrinkage test, all the samples were conditioned for 24 h. The fabric samples were subjected to domestic washing procedures. The shrinkage ratio R was calculated as follows:

$$R = \frac{S_0 - S}{S_0} \times 100\% \tag{1}$$

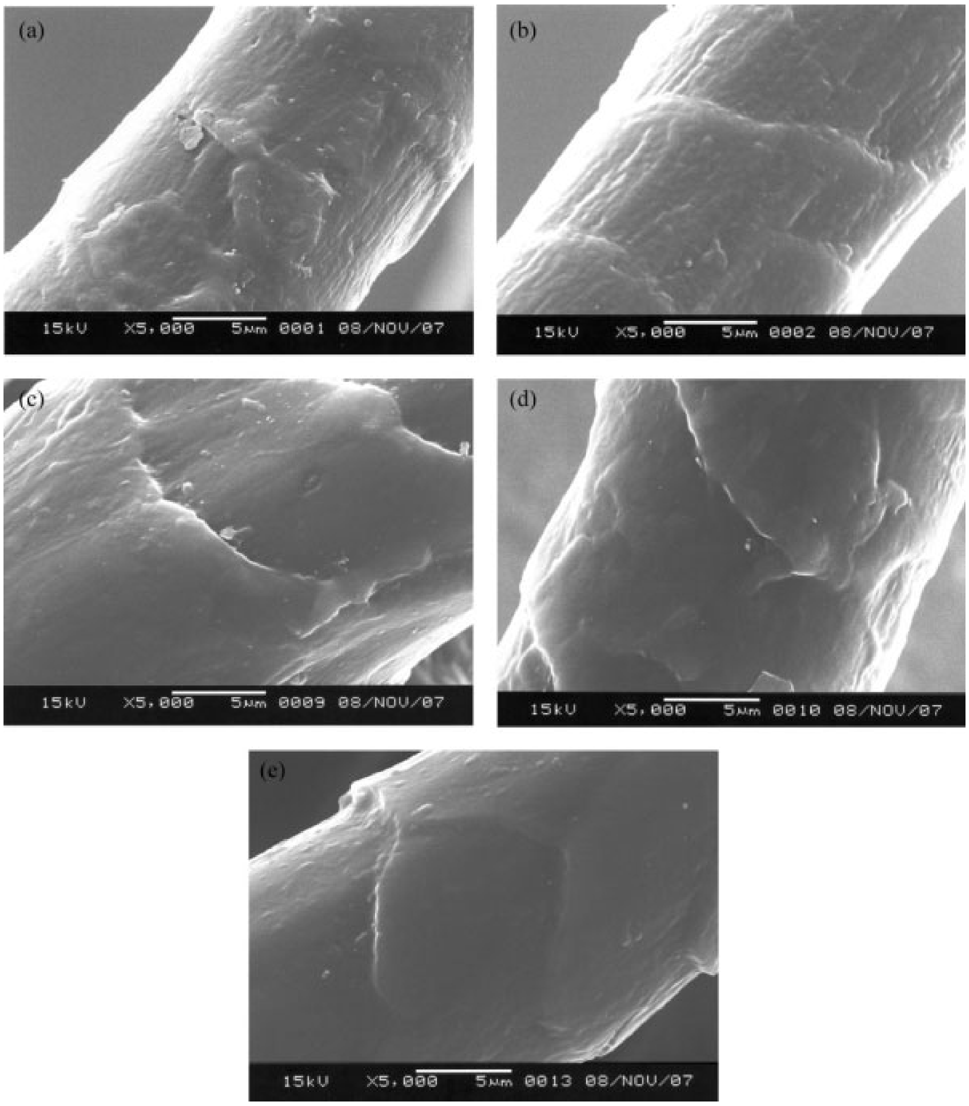

Figure 1 SEM micrograph of (a) 100% RH conditioned, He plasma treated, (b) 100% RH conditioned, He/O_2 plasma treated, (c) 65% RH conditioned, He plasma treated, (d) 65% RH conditioned, He/O_2 plasma treated, and (e) untreated.

where S_0 is the original fabric size, and S is the post-laundry fabric size.

RESULTS AND DISCUSSION

SEM analysis

On the surface of the fiber conditioned in 100% RH, most scales were removed in both pure He- and He/O_2-treated groups, and the fiber surface became much smoother (Fig. 1). However, scales of the 65% RH conditioned fibers were relatively intact under the same plasma treatment conditions. No significant difference was observed between the plasma-treated fibers using the two different gas mixtures, which could mean that plasma etching of wool may not be significantly influenced by the addition of O_2. However, oxygen in plasma treatment may play a more important role in chemical modification, as indicated in XPS analysis later.

Nearly complete peeling of scales on the surface of 100% RH conditioned wool fibers could be observed after plasma treatment. It could be attributed to the micro-deformation of wet wool fiber, leading to a much greater etching effect during bombardment of active species in plasma. Wool fiber could absorb large amount of water into hydrophilic cortex when conditioned in 100% RH environment. Breakage of intrafibril hydrogen bonds by absorbed water leads to swelling of the fiber bulk, while less deformation occurs in scale areas for its hydrophobicity. Differential deformation of these two parts resulted in increased scale angles to the fiber axis as shown in Ref. 20, and a larger area on the surface could be exposed to the plasma that facilitated plasma etching of scales.

TABLE I
Elemental Composition in Percentages and Atomic Ratios for Untreated and Plasma-Treated Wool Fibers

Samples	C	O	N	S	Si	O/C
Untreated	60.4	26.9	5.1	0.58	7.0	0.45
100%, He plasma	53.4	30.8	4.8	0.47	10.5	0.58
100%, He/O_2 plasma	53.3	33.9	3.3	0.24	9.3	0.64
65%, He plasma	52.5	31.5	5.3	0.80	9.9	0.60
65%, He/O_2 plasma	49.5	34.5	4.1	0.56	11.4	0.69

In 65% RH condition, the wool fibers that do not absorb as much moisture as those in 100% RH is similar to usual environment for usage and storage of wool, as a result, molecular structure of wool fiber was nearly unaffected. Less area was shown during plasma treatment when compared with those samples conditioned in 100% RH. As a result, surfaces of wool fiber conditioned in 65% RH were only partially etched and mostly unaffected.

XPS surface analysis

Concentration of surface elements of four treated samples and original sample were measured and summarized in Table I. The sulfur element detected on the surface was from thioester linkage among outmost lipid. The silicon on the surface was resulted from organic silicon-softening agent applied during previous finishing process.

It could be seen that C1s content decreased significantly after plasma treatment, and Ols content increased, which indicated the introduction of oxygen-contained groups on the fiber surface. The amount of N1s and S1s did not vary greatly after the plasma treatment, which is similar with results of other researchers.[25] As reported by Molina et al.,[16] the C1s peak for original wool fiber was from fatty acid of epicuticle, and the etching effect and the introduction of other chemical elements caused the reduction of percentage of carbon content.

Sulfur is a key element in thioester group, which plays a vital role in connecting epicuticle with endocuticle. Nitrogen is also an essential element in polypeptides of wool fibers. As shown in Table I, sulfur and nitrogen content did not change substantially for He plasma-treated groups, whereas for samples treated with He/O_2 plasma, sulfur and nitrogen content decreased significantly. This could be due to more severe oxidation of these fibers. Also, certain amount of silicon was detected on fiber surfaces, which could be resulted from the sizing applied for yarn spinning process. All the fibers had similar amount of silicon and thus its effect is not unique to any particular group.

The deconvolution analysis of C1s is shown in Figure 2, including concentration of different components containing C1s. From these figures, the amount of C—O groups were reduced on the fiber surface for the 100% RH conditioned groups, which could be the result of effective etching of outmost oxidized layer and larger exposure of lipid layer mainly composed of long-chain hydrocarbons. For the 65% RH conditioned groups, less effective etching lead to more oxidized parts remained on fiber surface, resulting in similar chemical compositions with untreated samples.

And between groups treated with different gases, more oxygen was introduced onto the surfaces for the samples treated with helium and oxygen. However, the difference in the amount of C—O groups and O=C—O groups was small between the samples conditioned in the same RH but treated with different gases. This could be attributed to the dominant role of plasma etching in the resultant surface chemical composition.

Single fiber wettability

As shown in Table II, the initial contact angle for the untreated wool fiber was significantly larger than the plasma-treated samples, which indicated that plasma treatment was effective in improving the wettability of wool fibers. For 100% RH conditioned groups, difference caused by different gas types was not significant. However, for 65% RH conditioned wool fibers, the addition of oxygen to the plasma further decreased the contact angle by 25%. These results agree with the literature. Molina et al.[26] have used dynamic water contact angle to characterize the wettability of human hairs before and after plasma treatment and found that the advancing contact angle for untreated and plasma-treated human hairs are 103° and 60°. Sun and Stylios[27] have measured the static water contact angle for wool fabrics and found that the water contact angles are 79.7° and 23° for untreated and plasma-treated fabrics. Our data is some what different from these published literatures because of the difference in measurement techniques, but the trend for the reduction of water contact angle after plasma treatments is the same.

Shrink resistance

The area shrinkage ratio of wool samples treated with APPJ with different conditions is presented in Table III. Compared with the untreated wool sample, the sample with different moisture contents showed a certain antifelting trend after atmospheric plasma treatment. Wool fabrics conditioned in 100% RH resulted in the lowest shrinkage ratio 5.2% after pure helium gas plasma treatment and 5.9% after helium and oxygen gas plasma treatment in accordance with the SEM results. Shrinkage ratios of 65% RH groups were 8.9% and 7.2% for pure He gas and

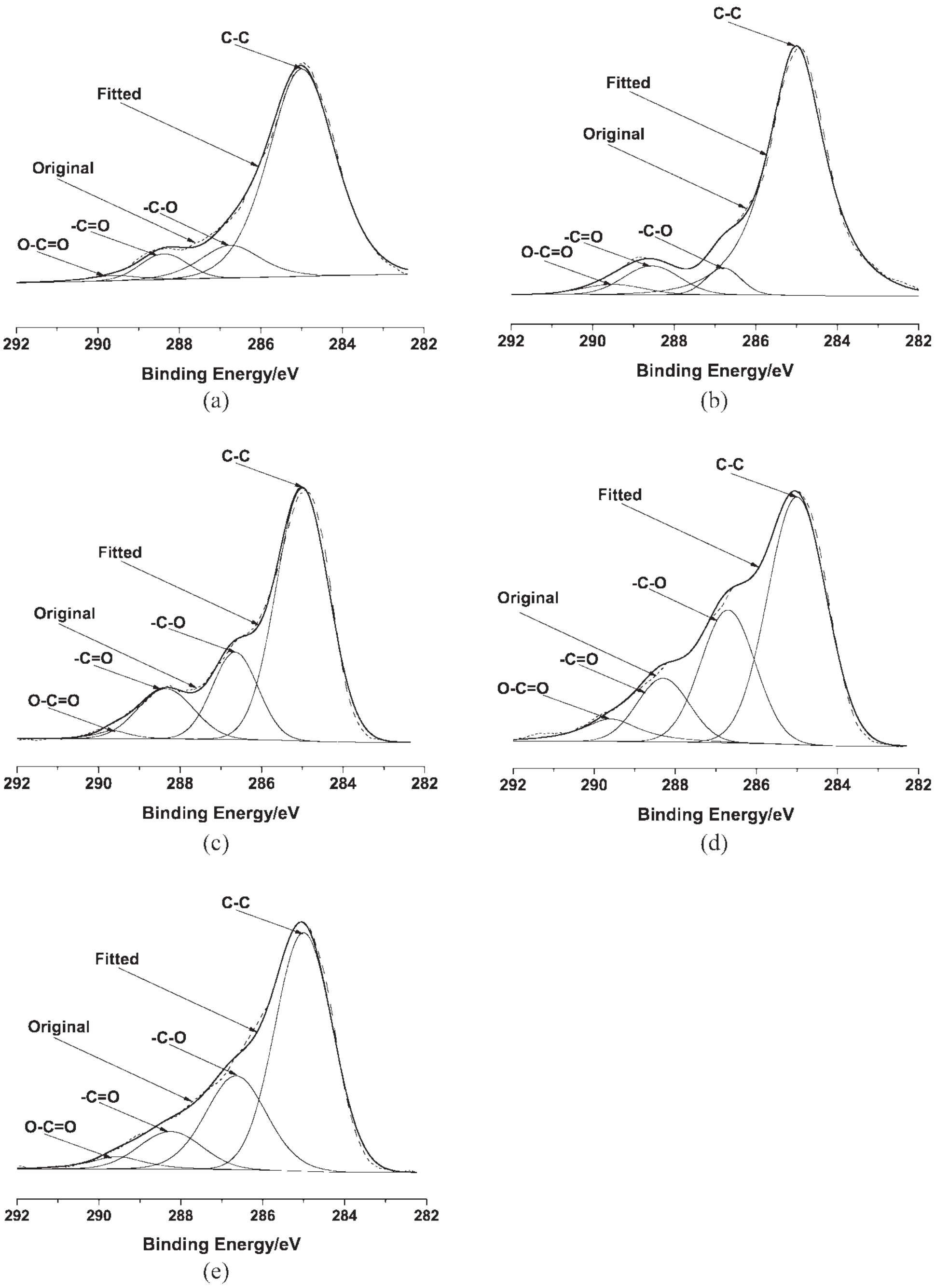

Figure 2 XPS Cls core-level spectral of the untreated and APPJ-treated wool fibers: (a) 100% RH conditioned, He plasma treated, (b) 100% RH conditioned, He/O_2 plasma treated, (c) 65% RH conditioned, He plasma treated, (d) 65% RH conditioned, He/O_2 plasma treated, and (e) untreated.

TABLE II
Water Contact Angles of Untreated and Plasma-Treated Wool Fabrics

Samples	Contact angle (°) Mean	Standard deviation
Untreated	49.3^{a*}	12.0
100%RH, He plasma	32.06^{bc}	7.1
100%RH, He/O_2 plasma	29.68^{bc}	6.4
65%RH, He plasma	37.32^{b}	7.7
65%RH, He/O_2 plasma	27.78^{c}	6.3

* Values with different letters are statistically significant at $P < 0.05$.

TABLE III
Area Shrinkage Ratios for Untreated and Plasma-Treated Wool Fabrics

Samples	Area felting shrinkage (%)
Untreated	10.9
100%RH, He plasma	5.2
100%RH, He/O_2 plasma	5.9
65%RH, He plasma	8.9
65%RH, He/O_2 plasma	7.2

He/O_2 gas treated, respectively. According to ISO 6330, knitted wool fabric is regarded as machine washable only when the area shrinkage is below 8%. Three types of plasma-treated samples could be considered as machine washable in this experiment.

The result could be attributed mainly to the morphological change on the wool fiber surface, while chemical modification of fiber surface played a minor role. With high moisture regain of wool fiber conditioned in 100% RH, microstructure of wool fiber changes greatly. Outer layer remains hydrophobic while inner layer swells because polypeptide chains absorb large quantity of water, and as a result, the angles between the fiber axis and scales become larger. The tips of the scales were standing out under plasma and significant etching effect could be seen for the 100% RH conditioned groups. On the other hand, the etching effect of the plasma treatment was restricted to a less exposed scale tip area for the 65% RH conditioned groups, resulting in a larger felting effect.

CONCLUSIONS

In this study, wool fibers and wool fabrics conditioned in different RH levels were treated by an APPJ with two types of gases, pure He and He/O_2 (10 : 1) mixed gas. The surface morphology, surface chemical composition analysis, and shrink resistance were examined as compared with those of the untreated wool. The following are the findings:

1. Atmospheric plasma treatment can effectively modify the surface of wool physically and chemically. After the treatment, scales of the surface were destroyed, chemical changes on the surface of wool fibers were significant. Water contact angle of wool was also reduced after plasma treatment and more so for wool fibers treated with He/O_2 plasma. Laundry shrinkage of wool fabrics after plasma treatment was reduced.
2. The moisture content of wool fiber during plasma treatments has a substantial influence on the treatment effect. For wool samples conditioned in 100% RH, almost a thorough removal of the scales was observed, accompanied by a significant change in fiber surface chemical compositions, resulting in the lowest area shrinkage ratios in shrinkage resistance test. For the tested fabric structure, the area shrinkage ratios for the 100% RH conditioned groups met the requirement of machine-washable fabrics in the ISO standard.

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