Effect on the Anti-Felt Properties of Atmospheric Pressure Plasma Treated Wool

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ABSTRACT: Wool fabrics were treated with air/helium and oxygen/helium atmospheric pressure plasmas. Wetting properties, anti-felt properties, solubility properties in an alkaline medium, and tensile strength loss of the wool fabric were measured. Surface morphology and chemical compositions of the wool fabric were analyzed using scanning electron microscopy and X-ray photoelectron spectroscopy, respectively. Both air/helium and oxygen/helium plasmas greatly improved wool shrink-resistance (11.67% and 10.98%, respectively) with very little damage to the wools, though plasma treatments alone could not reach wool fabric ''machine washable'' level of 8% shrinkage. The reason for the treated wool having higher anti-felt property was that the plasma treatments produced physical etching action to generate fiber surface cracks and induced the oxidation reaction to enrich oxygen and nitrogen on wool surface. The wool samples pretreated with atmospheric pressure plasma and subsequently treated with Synthappret BAP showed area shrinkages of 5.64% (air/helium) and 5.23% (oxygen/helium), and thus met the machine washable requirement. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1142–1146, 2008

Key words: wool; atmospheric pressure plasma; anti-felt; finishing

INTRODUCTION

Wool is regarded as a luxurious fiber because of its characteristics such as ability to be shaped by heat and moisture, good moisture absorption without feeling wet, excellent heat retention, water repellency, and flame-retardant. However, wool has the undesirable properties of felting and shrinking under certain conditions, such as moisture, heat and mechanical agitation, because of its morphological structure and scale surface composition. All textiles made of untreated wool tend to felt in regular machine washing conditions. Nowadays wool products are expected to show the same easy-care properties as articles made of manmade fibers. Many methods have been developed to reduce the felting of wool, and many successful commercial shrink-proofing processes are now available. However, because of the presence of a high degree of disulphide cross-linkage in the A-layer of the exocuticle and the fatty acids on the fiber surface, wool fiber generally is hydrophobic in nature.[1–3] Such complicated surface structure provided a surface barrier against chemicals diffusing into wool.[4] Typical shrink-resistant treatment processes of wool combine degradation of scale with chloro-organic compounds and application of a resin.

Effluents from wool finishing processes can be an environmental hazard with a variety of harmful substances such as chloro-organic compounds or heavy metals from anti-felt finishing and dyeing processes.[5] Therefore, the development of wool modification and finishing treatments by environmentally friendly processes are urgently needed. Plasma treatments appear to be promising options for such processes.[6]

Some studies on the effect of plasma treatments on wool have shown that it leads to improved printability and dyeability with acid dyes as well as reduced felting.[7–10] Surface analyses of wool treated with plasma have shown that the content of the hydrophilic groups increases and part of the

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cystine in the surface layer is converted to cysteic acid.[11]

In most published papers up to now, plasma treatments in wools were carried out under low pressure or high vacuum. However, low-pressure plasma treatment is most likely a batch process that is time, energy, and space consuming and may not be economically feasible for most of the textile products. Meanwhile, the density of activated particles is relatively low because of high vacuum. To overcome these drawbacks of low-pressure plasma treatments, atmospheric pressure plasma treatments have been introduced to treat materials continuously with higher activated particle density and a temperature below 40°C.

In this article the effects of atmospheric pressure air/helium and oxygen/helium plasma on wool were investigated. Water penetration, solubility in alkaline medium, tensile strength, and laundry shrinkage of the plasma treated wool fabrics were measured. The wool fiber surface morphology was examined by scanning electron microscopy (SEM) and the surface chemical composition change of the plasma treated wool was analyzed using X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Wool Jersey Knit Fabrics with 205 g/m^2, 1.32 m (52 in.) in width was supplied by Testfabrics, USA. The wool samples were scoured with dichloride methane for 24 h by Soxhlet extraction. The solvent scoured wools were washed twice with 98% alcohol and rinsed twice with deionized water. The fabrics were dried in an oven at 50°C for 30 min and then air dried.

For the plasma treatment, the wool specimens were placed in the chamber of an atmospheric pressure plasma treatment devise.[12] The treatment conditions and machine parameters were the same as those in our previous study.[12] In the process, a specimen was laid on a frame and then inserted into the plasma chamber once the plasma was stabilized. The samples were treated by air/ helium or oxygen/helium plasmas for different durations.

Synthappret BAP was applied by dip-pad-dry method. The plasma treated wool samples were two-dipped-two-nipped in a finishing bath containing 15 g/L Synthappret BAP, 2 g/L sodium bicarbonate with a pick up of 100 ± 5%. The padded samples were dried at 100–105°C and then cured at 135°C for 1 min.

Wettability of wool was evaluated by measuring the time required to adsorb 1 μL of distilled water.

Shrink resistance during washing test was performed according to the International Wool Secretariat (IWS) TM31, using two 5A cycles to assess felting shrinkage. When the area shrinkage was lower than 8% after two 5A cycles, the wool is regarded as ''machine washable.''

Solubility of wool sample in alkaline was measured according to ISO 3072-1975. NaOH of 0.1 mol/L concentration and bath temperature of (65 ± 0.5)°C were employed in the experiment. Before the experiment, the wool samples were extracted by dichloromethane for 1 h.

Tensile tests of the wool fabrics were conducted according to ASTM standard method D-5035. The fabrics were cut into 15.24 × 5.08 cm^2 (6 × 2 in.) pieces, and three specimens were tested for each treatment group. The tests were carried out at 20°C and 65% relative humidity. Compared with the control, the tensile strength losses of the plasma treated wool samples were calculated.

XPS analysis of wool was performed on a Perkin Elmer PHI 5400 system. Each specimen was scanned five times with a pass energy of 35.75 eV, a working function of 4.4 eV, and 1 eV/step.

The surface morphology of wool was observed using a HITACHI S-3200N SEM. The specimens were gold sputter coated for 150 s with a thickness of ~250 Å.

RESULTS AND DISCUSSION

Water penetration of wool

The time required for water penetration of wool treated with atmospheric pressure plasma is shown in Table I. It is apparent that the time of water penetration into wool greatly decreased after air/helium or oxygen/helium plasma treatment. This might be due to water molecules absorbance and diffusing relatively quickly into the treated fiber as a result of surface modification, such as physical etching to produce crack and chemical reaction to introduce hydrophilic groups. The oxygen/helium plasma treated sample adsorbed water more quickly compared with the air/helium plasma treated one. It is likely that the increase in hydrophilic properties of oxygen/helium plasma treated wool was largely because of the incorporation of more oxygen atoms on the fiber surface.

TABLE I
Wettability and Solubility of Wool Untreated and Treated with Atmospheric Pressure Plasmas

Treatment	Time of water penetration (s)	Solubility rate (%)
Untreated	>2000	25.72
Air/helium plasma	2	25.68
Oxygen/helium plasma	<1	25.34

TABLE II
Tensile Strength Loss of the Wool Treated with Atmospheric Pressure Plasmas

Samples	Tensile strength loss (%)
Air/helium plasma	3.45
Oxygen/helium plasma	4.85

Solubility of wool in an alkaline solution

The solubility of the plasma-treated wool in an alkaline solution is a useful parameter for estimating wool scathe. Also from Table I, the solubility of plasma treated wools was similar to that of the untreated sample. Therefore both air/helium and oxygen/helium atmospheric pressure plasma treatments brought very little damage to the wool. This is consistent with the fact that plasma treatment affects only the fiber surface rather than the bulk properties of fibers.[12]

Tensile strength

To test the effect of plasma on its mechanical properties, tensile strengths of the wool fabric after the plasma treatments were measured and presented in Table II. The plasma treatments result in tensile strength losses of only 3.45% for air/helium and 4.85% for oxygen/helium plasma treated samples. This further indicated that the air/helium and oxygen/helium atmospheric pressure plasma treatments most likely etched only the scales of the wool fibers. In general, the tensile strength of the fabric depends on not only fiber strength but also many other factors such as fabric structure, yarn twist, and yarn count. Atmospheric pressure plasma treatments do not alter the fabric structure but only cause surface roughness change of the fibers. The tensile properties such as tensile energy, resilience and extensibility of the treated wool fabrics may be slightly changed because of the increase of surface frictional characteristics as reported by Kan and Yuen.[13]

Anti-felt properties of wool

The area shrinkage values of wool samples untreated and plasma treated for different durations are shown in Figure 1. The area shrinkages of both air/helium and oxygen/helium plasma-treated wool showed a significant reduction compared with the untreated sample. When the plasma exposure time was less than 3 min, the area shrinkages of the samples were decreased greatly with the increase of the treatment time, but changed little afterwards. With plasma exposure time of 3 min, the area shrinkages of the wool fabrics were 11.67% (air/helium) and 10.98% (oxygen/helium), still more than 8%, showing that either air/helium or oxygen/helium plasma treatment alone might not be able to reach ''machine washable'' level with the current experimental conditions.

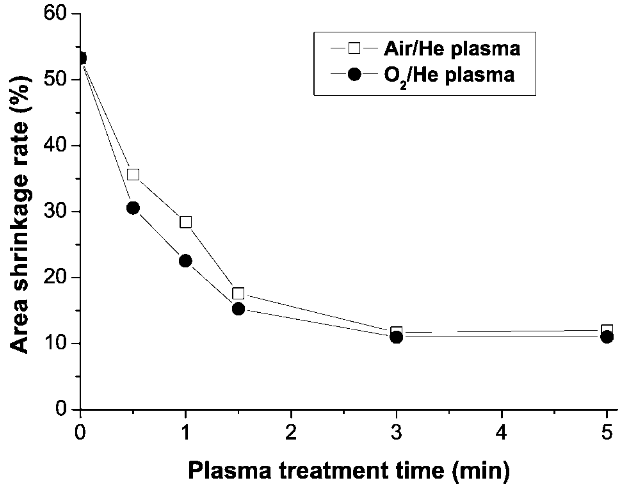

Figure 1 The relationship between area shrinkage of wool and plasma exposure time.

Synthappret BAP finishing agent is used for articles made of wool and wool blends for anti-felt finishing application without prechlorination, improved area stability, stretch capacity and elastic recovery, reduced pilling and snagging, and improved resistance to abrasion. However, the area shrinkage value of wool finished by Synthappret BAP was 17.5% (see Table III), far above 8%, suggesting that the finishing agent itself could not meet the ''machine washable'' requirement. On the other hand, the plasma treatment combining with Synthappret BAP finishing clearly produced a shrink-resist effect. After the atmospheric pressure plasma pretreatment and subsequent Synthappret BAP finishing, the area shrinkages of wool samples were 5.64% (air/helium) and 5.23% (oxygen/helium), respectively, lower than 8%.

Wool surface morphology

SEM images of wools untreated and treated with air/helium and oxygen/helium atmospheric pressure

TABLE III
Area Shrinkage of Wool Untreated, Treated by Plasma or Resin Alone, and Plasma + Resin[a]

Treatment	Area shrinkage rate (%)
Unfinished	53.3
Resin finished	17.5
Air/He plasma treated + BAP resin finished	5.64
O_2/He plasma treated + BAP resin finished	5.23

[a] Plasma exposure time 3 min; Syhthappret BAP concentration 15 g/L.

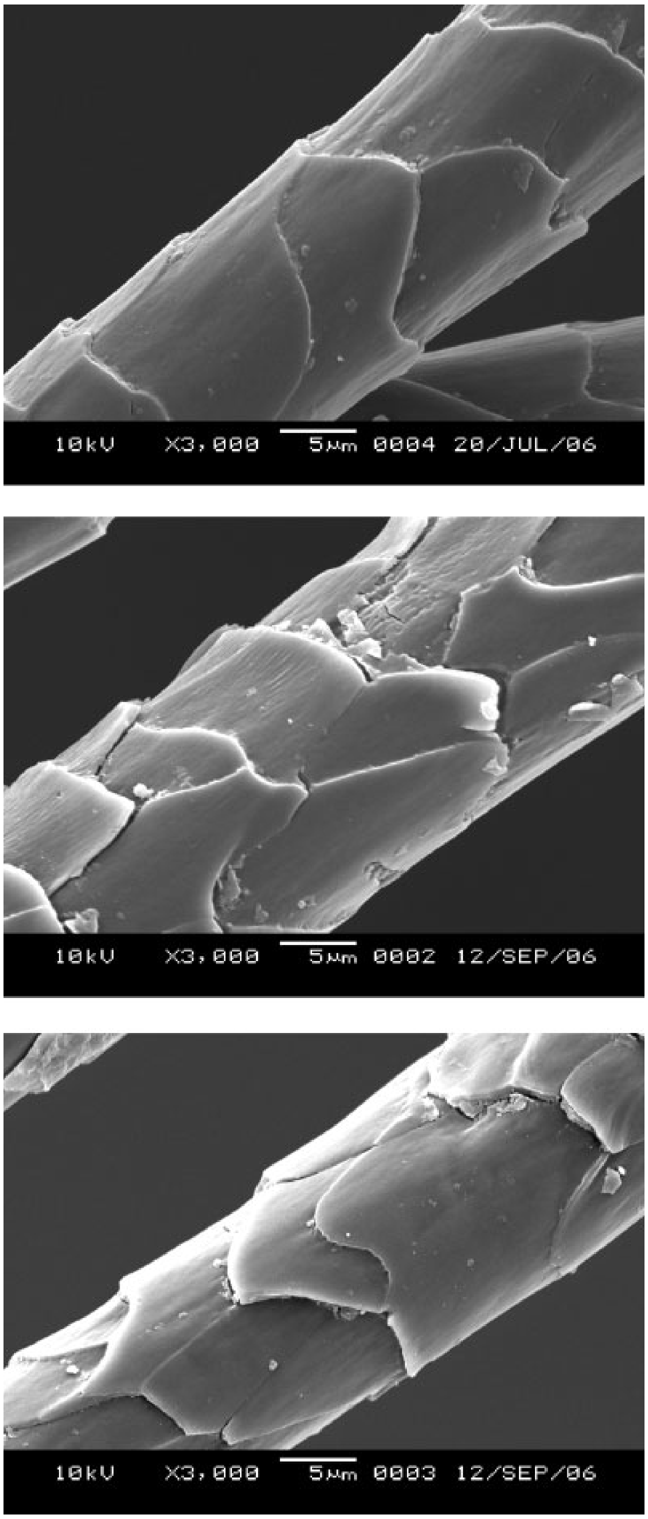

Figure 2 SEM photographs of the wool fibers (with magnification ×3K) (top) Untreated; (middle) Air/helium plasma treated; (bottom) Oxygen/helium plasma treated.

plasma treatments are illustrated in Figure 2. Certain degrees of plasma etching effect on the surface of wool are shown compared with the untreated one, namely some cracks and damaged edges of scales appeared on the plasma-treated wool fiber surfaces. Such etching and cracks may help to eliminate the surface barrier of the wool fiber, dramatically reducing water penetration time and enhancing anti-felting property.

XPS analysis of wool surface composition

Table IV shows the relative intensities of C_{1s}, O_{1s}, N_{1s}, and S_{2p} in XPS measurements of the wool with or without the plasma treatments. The carbon intensities of the wool decreased 4.1% after air/helium plasma treatment and 14.5% after oxygen/helium plasma treatment. The oxygen intensity increased 20.3% and 53.5% with air/helium and oxygen/helium plasma treatments. Meanwhile, the O/C ratio increased 25.1% and 79.5% after air/helium and oxygen/helium plasma treatments, respectively. These results indicated both air/helium and oxygen/helium plasmas induced oxidation reactions and incorporated oxygen atoms on the wool surface, and oxygen/helium plasma had a more profound effect than air/helium plasma. The nitrogen intensity was also increased somewhat which could be a result of enrichment of nitrogen because of redeposition of fragmented polymer chains during etching.

Relative peak areas of the components by deconvolution of C spectra are summarized in Table V. The C_{1s} spectra of wool treated by atmospheric pressure plasma may be separated into several subcomponents, of which the peak at 285 eV corresponds to —C—C, —C—H, the peak at 286.3 eV corresponds to —C—O—, —CN—, and the peak at 289 eV corresponds to —CON—, —COO—. The intensity of the —C—C, —C—H peak decreased 4.8% with air/helium atmospheric pressure plasma treatment, and 14.3% with oxygen/helium plasma. The —C—O—, —CN— peak intensities increased 5.1% and 31% with air/helium and oxygen/helium plasmas, respectively. The —CON—, —COO— intensities were enhanced 34% and 82% with air/helium and oxygen/helium plasma treatment, respectively. These phenomena are mainly because of the oxidation of the wool with the plasma treatments, resulting in a decrease of —C—H and —C—C— bonds and an increase of —C—O—, —CN—, —CON—,

TABLE IV
Relative Intensities of the Surface Chemical Composition of Wools Untreated and Treated with the Atmospheric Pressure Plasmas

Treatment	Chemical composition of surface (%)				
	C_{1s}	O_{1s}	N_{1s}	S_{2p}	O_{1s}/C_{1s}
Untreated	78.4	11.8	7.2	2.6	15.1
Air/He plasma 3 min	75.2	14.2	8.3	2.3	18.9
O_2/He plasma 3 min	64.3	21.8	11.8	2.1	33.9

TABLE V
Relative Peak Areas of C_{1s} Spectrum of Wools Untreated and Treated with the Atmospheric Pressure Plasmas

Binding energy (eV)	XPS-data element	Relative peak of chemical component (%)		
		Untreated	Air/He	O_2/He
285	—C—C—, C—H	78.9	75.1	67.6
286.3	—C—O—, —CN—	11.7	12.3	15.3
289	—CON—, —COO—	9.4	12.6	17.1

and —COO— bonds, directly leading to an increase in surface tension and wettability. This was also one of the reasons why the plasma treated wools had a much higher water penetration speed and anti-felt effect.

CONCLUSIONS

The effects of atmospheric pressure plasma treatment on a wool fabric were studied in terms of its water penetration, solubility in alkaline medium, tensile strength, and laundry shrinkage. The time required for water penetration into the wool fabric was greatly shortened after it was treated with both air/helium and oxygen/helium atmospheric pressure plasmas. For plasma exposure of 3 min, the area shrinkages of the wool treated with air/helium and oxygen/helium plasmas were 11.67%, and 10.98%, respectively, above ''machine washable'' level of 8%. However, the wool samples pretreated with atmospheric pressure plasma and subsequently treated with Synthappret BAP showed area shrinkages of 5.64% (air/helium) and 5.23% (oxygen/helium), respectively, and thus met the machine washable requirement. The solubility of the plasma treated wools was similar to that of the untreated samples and the tensile strength of the treated fabrics decreased only 3.45 and 4.85%, indicating the atmospheric pressure plasma treatments caused very little damage to the wool fabrics. Both air/helium and oxygen/helium atmospheric pressure plasma treatments were effective in modifying wool surface through etching to produce cracks and chemical reactions to incorporate oxygen and nitrogen onto wool surface, resulting in more hydrophilic surfaces and significant anti-felt properties.

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