Dyeing Properties of Wool Fabrics Treated with Atmospheric Pressure Plasmas

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ABSTRACT: The dyeing properties of wool treated with atmospheric pressure plasma are investigated in terms of exhaustion with dyeing time, absorption isotherm and C_t/C_∞ versus $t_{1/2}$ curves, dyeing rate (half-dyeing time), exhaustion at dyeing equilibrium, and color fastnesses. The wettablity and surface morphology of the plasma-treated wool are also analyzed. Through both air/helium and oxygen/helium atmospheric pressure plasma treatments, the water contact angle of the fabric decreases from 132.4° to 0° and water penetration time drops from more than 2000 s to 1 s or 2 s. The scanning electron microscopy analysis shows etching and crack marks on treated fiber surfaces. The plasma treatments greatly increase initial dyeing rate, shorten half-dyeing time, $t_{1/2}$, and the time to reach dyeing equilibrium, although the final exhaustion and color fastnesses do not change. The Langmuir adsorption equation is also valid for the plasma-treated wools dyed with an acid dye. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1257–1261, 2008

Key words: wool; atmospheric pressure plasma; dyeing; acid dye

INTRODUCTION

Effluents originating from wool dye houses, including chloro-organic compounds from antifelt finishing and dyeing processes and heavy metals from dyeing, pollute the environment and water resources.[1] Ecologic and economic restrictions which are increasingly imposed on the textiles industry require the development of environment-friendly and economic processes. Physical–chemical methods modify the surface of textiles without changing the nature of the bulk of the substrates, as well as with no ecological and economic problems. Plasma treatment is one promising approach of these methods. The plasma technique uses electric discharge and chemicals to diminish water consumption and since it is a dry system in textile processing. Therefore, significant amount of efforts have been made in surface modification of textiles with plasma techniques, especially low pressure plasmas, including improving wetting, adhesion, color, and dyeing properties.[2–5] For textile processes, due to the nature of the materials, namely large quantity and hygroscopic, low pressure plasmas are not effective since pulling vacuum for such materials consumes lot of time and energy, which greatly restricted the application of the technique in textiles. Atmospheric pressure plasmas, on the other hand, can be directly used on line in textile processes without creating vacuum and therefore are more suitable for textile materials.

The promotion effect of plasma treatments in wool dyeing has been studied.[6–9] However, most of the research projects have used low pressure plasmas. Little has been reported in application of atmospheric pressure plasmas in wool dyeing. In this article, we have treated wools with both air/helium and oxygen/helium atmospheric pressure plasmas and subsequently dyed them with an acid dye (Folan Fast Navy Blue 5R). The effects of the plasma treatments on wool dyeing properties have been studied including dyeing rate (half dyeing time $t_{1/2}$), exhaustion, dye absorption isotherm, and color fastnesses, as well the wetting properties and surface morphology of the plasma-treated wools are discussed.

EXPERIMENTAL

Materials and Chemicals

Wool Jersey Knit Fabrics with 205 g/m^2, 132 cm in width was supplied by Testfabrics, Inc, USA. The

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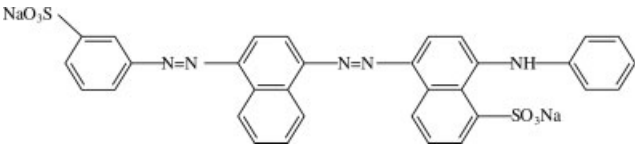
TABLE I
Wetting Properties of the Wool Fabrics

Treatment	Contact angle (°)	Time of water penetration (s)
Untreated	132	>2000
Air/helium plasma	0	2
Oxygen/helium plasma	0	<1

Both air/helium and oxygen/helium plasma exposure time was 3 min.

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 fibers were dried in an oven at 50°C for 30 min and then air dried.

Folan Fast Navy Blue 5R (C.I. Acid blue 113) with a structure as following was supported by Ciba Specialty Chemicals Ltd.



The commercial dye sample was purified first by dissolving in hot sodium acetate-alcohol mixture solvent and then filtering. The filtrate was precipitated with acetone, and the dye was finally collected and dried. All other chemicals used in the experiments were of analytical grade.

Plasma treatment

For the plasma treatment, the wool specimens were placed in the chamber of an atmospheric pressure plasma treatment device.[10] The treatment conditions and the machine parameters were the same as those in our previous publication.[10] In the process, a specimen was laid on a frame and inserted into the plasma chamber once the plasma was stabilized.

Wettability test

Wettability of the fabric was characterized as water contact angle which was measured using a goniometer (Model A-100 by Ramé-Hart) with a telescope, by the sessile drop technique. The contact angles were measured in five different places for each sample.

Surface morphology observation

The surface morphology of wool was observed with a HITACHI *S*-3200N Scanning Electron Microscope. The specimens were gold sputter coated for 150 s with a thickness of approximately 250 Å. Pictures were taken with beam energy of 5.0 keV.

Dyeing process

Dyeing behavior of the wool sample was investigated including the exhaustion, absorption isotherm and C_t/C_∞ versus $t_{1/2}$ curves (C_t and C_∞ are dye concentrations at time t and equilibrium respec-

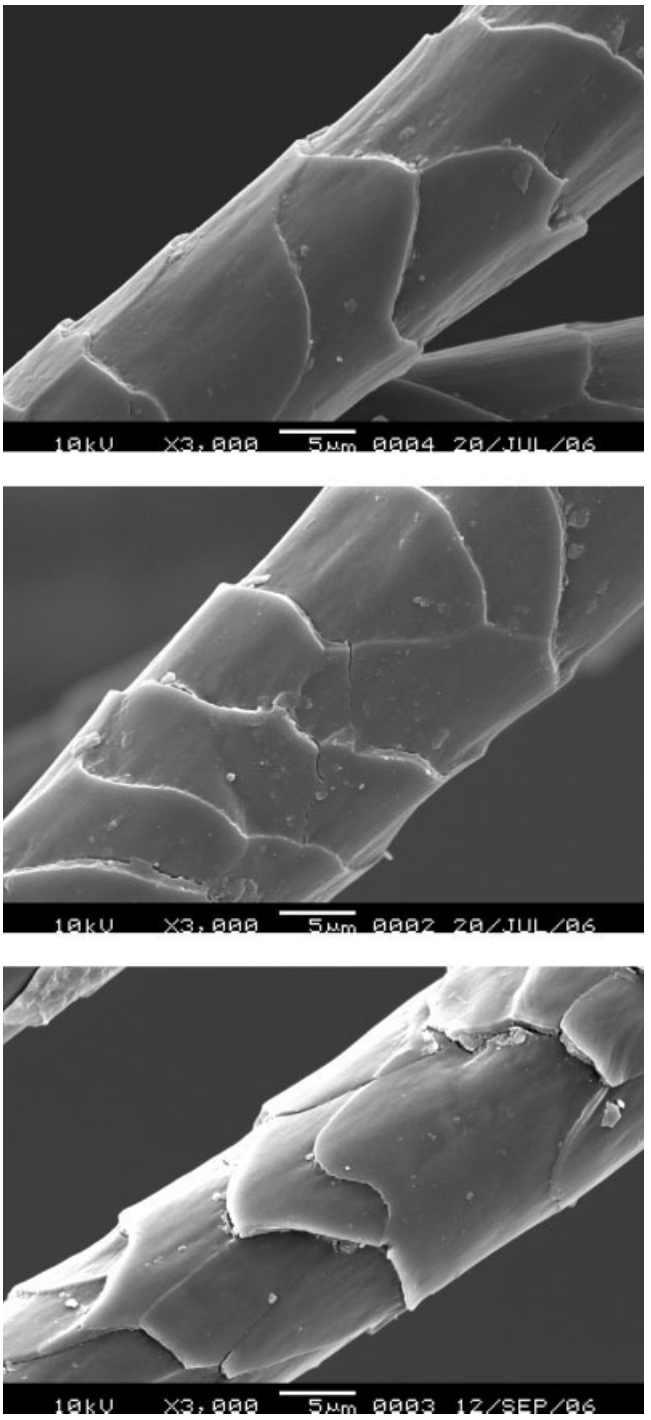


Figure 1 SEM pictures of wools treated by atmospheric pressure plasma (with a magnification of 3.0 k). (Top) Control; (middle) air/helium plasma 3 min; (bottom) oxygen/helium plasma 3 min.

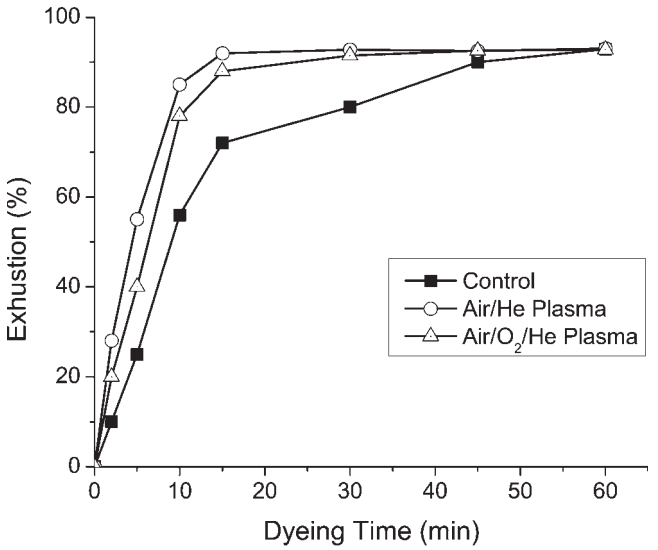


Figure 2 Relationship between dyeing time and dye exhaustion of wool fabrics.

tively), dyeing rate (half dyeing time), and exhaustion at dyeing equilibrium.

The dyeing process was carried out in an oscillating sample machine. Wool samples were dyed with 2% (O.W.F) and 20 g/L sodium chloride at a liquid-to-goods ratio of 100 : 1. The dyeing system was maintained at pH 4 using 0.05*M* sodium acetate with proper amount of acetic acid. The dye bath was kept at a temperature of 90°C for definition time (explained in text). The quantity of dye taken up by the wool sample exhaustion was determined from the difference in light absorbency of the original and exhausted dye bath solutions at different times of dyeing. The light absorbency of the dye was measured at the wavelength of maximum absorption using a 2100 Spectrophotometer. All measurements of the dye solution were conducted at room temperature and the percentage exhaustion was calculated according to the following equation:

$$E = \left(\frac{A_0 - A_t}{A_0}\right) \times 100\%, \quad (1)$$

where E is the percentage exhaustion at time t, A_0, and A_t are the absorbance of dye solution at 0 min and time t, respectively.

Time of half-dyeing time $t_{1/2}$ calculated from the exhaustion curves was the time taken for the samples to absorb 50% of the dye at equilibrium.

Dye concentration in fiber $[D]_f$ and bath $[D]_s$ testing

Dye concentrations in fiber $[D]_f$ were measured by extracting the dye from the fiber with 25% aqueous pyridine solution, and dye concentrations in bath $[D]_s$ were determined photometrically after dyeing. The wools were dyed at 90°C for 2 h with initial dye concentration of 5×10^{-4} Mol/L.

TABLE II
Half-Dyeing Times and Percentage Exhaustion at Equilibrium of Wool Fabrics

Sample	Half-dyeing $t_{1/2}$ (min)	Exhaustion at equilibrium (%)
Control	10.06	92.89
Air/helium plasma	5.19	93.03
Oxygen/helium plasma	4.83	92.78

Color fastness measurement

Color fastnesses were tested according to the AATCC Test Methods 107-1997 (Color Fastness to Water Washing); 15-1997 (Color Fastness to Perspiration); and 120-1994 (Color Change to Flat Abrasion). The Gray Scales were used for measuring color change and staining on the multifiber fabrics under the illumination of D65.

RESULTS AND DISCUSSION

The contact angles and time required for water penetration of wool treated with atmospheric pressure plasma and the control are listed in Table I. As shown in Table I, it is clear that through atmospheric pressure plasma treatment, the contact angle of wools to water decreased from 132° to 0°. Furthermore, the time of water penetration into wool greatly decreased after both air/helium and oxygen/helium plasma treatments. This might be due to better water molecule absorbance and faster diffusing into the

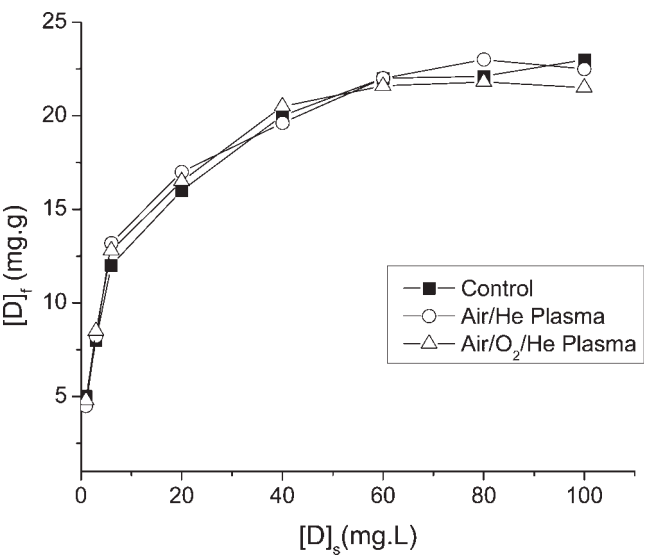


Figure 3 Adsorption isotherm curves of the wool fabrics.

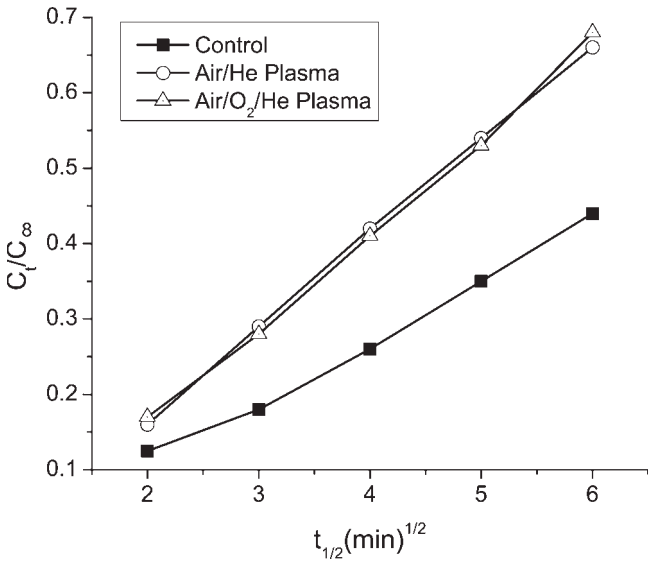


Figure 4 Relationship between $t_{1/2}$ and C_t/C_∞ of the wool fabrics.

treated fiber as a result of plasma surface modification, such as physical etching to produce microcracks and chemical reaction to improve hydrophilicity. The oxygen/helium plasma-treated sample adsorbed water more quickly compared with the air/helium plasma-treated one, indicating that the increased hydrophilicity of oxygen/helium plasma-treated wool is largely due to the incorporation of more oxygen atoms, resulting in more hydroxyl groups or carbonyl groups on the fiber surface introduced by the treatment with oxygen rich environment.

Figure 1 shows SEM pictures of plasma-treated and control wool fibers. It clearly shows the plasma etching effect on the surface of wool fibers as compared to the control fibers. Some microcracks appeared on the plasma-treated wool fiber surface, indicating that the plasma treatments did cause some physical alteration in the epicuticle layer of the fibers. It is likely that such etching and microcracks might help to eliminate the hydrophobic surface barrier of the wool fiber, dramatically reducing water penetration time and enhancing initial dyeing rate.

The percentage exhaustion curve shows the variation of dye bath concentration against time from which the characteristics of a dyeing system can be determined. Figure 2 illustrates the percentage exhaustion curves of atmospheric pressure plasma treated wools and the untreated sample (control) dyed by Folan Fast Navy Blue 5R. It is obvious that the slopes of the curves of plasma-treated fibers at the beginning of dyeing are steeper than that of the control, indicating a high initial dyeing rate. The oxygen/helium plasma treatment was more effective in increasing initial dye exhaustion than air/helium plasma. In addition, the time to reach the dyeing equilibrium for the plasma-treated wool fabrics was also shorter than that for the control. It was proposed that dyeing penetration into wool is not transcellular diffusion through the epicuticle surface, but inter cellular diffusion between the scales.[11,12] In this study, atmospheric pressure plasma was able to create microcracks on the surface of the scales (Fig. 1) and thus can indeed allow dye molecules to penetrate the fiber through the scales, making intercellular diffusion possible and contributing to accelerated dye diffusion.

The results of the half-dyeing time $t_{1/2}$ and percentage exhaustion at equilibrium obtained from Figure 2 are summarized in Table II from which, it is clear that half-dyeing time $t_{1/2}$ was significantly shortened by the atmospheric pressure plasma treatments, indicating a higher dyeing rate. However, the equilibrium exhaustion was not significantly different. This is because the plasma actions are confined to less than 100 nm layer of the wool fiber. Therefore most of the available dye sites remain almost unchanged through plasma treatment, with little effect on equilibrium exhaustion.

The dye adsorption isotherms for wool treated with atmospheric pressure plasma and the control are shown in Figure 3. For both air/helium and oxygen/helium plasma-treated wool dyed with an acid dye (Folan Fast Navy Blue 5R), the Langmuir adsorption equation is also valid, which is another indication of the fact that the plasma treatments are confined to a very thin layer of the wool fibers.

Figure 4 illustrates the relationship between C_t/C_∞ and $t_{1/2}$ of atmospheric pressure plasma-treated wools and the control. It is obvious that the C_t/C_∞ versus $t_{1/2}$ curves of all three wools have linear relationships. The slope that corresponds to the apparent diffusion coefficient of dye into wool increases significantly with both air/helium and oxygen/helium plasma treatments, indicating the

TABLE III
Color Fastness of the Dyed Wool Fabrics (Unit: Grade)

Sample	Washing			Perspiration			Abrasion	
	Change	Staining wool	Staining cotton	Change	Staining wool	Staining cotton	Dry	Wet
Control	4-5	5	5	4-5	4-5	5	4-5	4
Air/He	4-5	4-4	4-5	4-5	5	5	4-5	4
O_2/He	4-5	5	4-5	4-5	5	4-5	4	4

plasmas decreased the barrier effect in wool dyeing. The reason might be that the plasmas caused etching and chemical reaction, leading to relaxation of the cell membrane complex (CMC) and increased hydrophilicity of the wool, and resulting in dye diffusion through the intercuticle of the wool fiber surface more easily.

Table III shows the color fastness of the control and plasma-treated wool fabrics. After either air/helium or oxygen/helium atmospheric pressure plasma treatments, the color fastnesses to washing, perspiration, and abrasion were almost unchanged.

CONCLUSIONS

For wools dyed with the acid dye, both air/helium and oxygen/helium atmospheric plasma treatments increased initial dyeing rate, shortened time to reach dyeing equilibrium, but had little effect on final dye exhaustion. The dye absorption isotherm of the plasma treated wool fabrics also followed Langmuir law. The color fastness to washing, perspiration, and abrasion of the fabrics were not influenced by the plasma treatments.

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