Surface Functionalization of Wool Using 172 nm UV Excimer Lamp

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ABSTRACT: Wool is an important natural fiber having a complex surface structure which makes it difficult to dye and process it. It has a hydrophobic surface due to the presence of disulphide cystine crosslinks and a layer of fatty acids on the fiber surface. Conventional chemical treatments used to improve the hydrophilicity of wool often have an adverse effect on the feel and handle of this fiber. In this study, effect of monochromatic UV excimer radiation of 172 nm on the performance properties such as wetting, surface chemistry and surface morphology of wool has been studied. Irradiation reduces the wetting time of wool nearly by a factor of 10, even after a short exposure time of 1 minute, irrespective of the atmosphere used. Wetting time continues to decrease with increasing time of exposure and at 15 min of exposure, the absorption becomes instant. However, no significant change was observed in the ATR spectra of treated and untreated samples. SEM images show ablation and etching of the surface. The well defined scaly contour is not seen and there are deep striations on the surface of samples treated in nitrogen atmosphere. In case of samples exposed in O_2 atmosphere, micropores can be seen on the surface. Samples treated in nitrogen atmosphere for 15 min show nearly 100% exhaustion of acid dye as compared to 73% for untreated samples after 20 min of dyeing. Treated wool shows increased saturation dye uptake as well as improved rate of dyeing. Since these changes are restricted to surface and do not affect the bulk properties, these findings can have a significant effect on the commercial dyeing and finishing procedures used for wool and can be used to design cleaner and more efficient processes in future. J Appl Polym Sci 117: 3448–3453, 2010

Key words: dyes; surface modification; proteins; textile; UV excimer

INTRODUCTION

Wool is an important natural textile fiber but has a complex surface structure which makes it difficult to dye and process it. It has a hydrophobic surface due to the presence of a large number of disulphide cystine crosslinks in the exocuticle and a layer of fatty acids on the fiber surface. Together, these act as a barrier against penetration of dyes and chemicals into the fiber. Several chemical treatments such as chlorination have been developed to enhance the hydrophilicity of wool surface, but these treatments often use harsh chemicals which affect the fiber properties adversely and also are polluting in nature.

In the last few years, several studies have been undertaken on use of low temperature plasma (LTP) as a physical method for modifying the surface properties of wool. Treatment with O_2 plasma increases the surface free energy and enhances the wetting and wicking behavior of wool.[1] It has been shown[2] that O_2 plasma leads to enhanced saturation dye uptake as well as a faster rate of dye uptake by treated wool when dyed with acid, reactive and chrome dyes. These effects are attributed to the change in the morphology of wool surface due to creation of microcraters or striations as well as partial modification of the scale structure on irradiation. Chemistry of the fiber surface also gets modified due to development of groups such as —C=O, C—O, and —COOH and NH_2. An increase in the nitrogen content and a decrease in the carbon and sulphur content on the surface is observed in the XPS analysis.[3] Presence of other polar groups such as cysteic acid and sulphonic acid, created due to the cleavage of cystine linkages has also been established.[4]

The encouraging lab results obtained with plasma treatment are difficult to replicate at industrial scale due to the limitations of plasmas with respect to consistency and uniformity of treatment in continuous processing. A more effective alternative can be the UV excimer lamps which are very promising for surface modification of textiles for large area industrial applications.

UV irradiation has recently been used to modify the surface properties of silk fiber to increase the hydrophilicity of silk[5,6] and creation of interesting

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multifunctional effects.[7] Hydrophilicity of polyester can be enhanced significantly and it can be dyed with basic dyes due to creation of anionic groups-COOH on the surface after UV irradiation.[8] Surface properties of wool fibers modified using wet chemical chlorination, laser, O_2 plasma and UV ozone have been compared.[9] Maximum values for surface oxygen were observed for UV treatment and 100% of surface sulphur was oxidised to S^{VI} state which was much better than all other methods used. However, there is scant literature available on the effect of UV excimer radiation on wool fiber.

In the current study effect of 172 nm UV excimer radiation on the properties of wool fiber have been reported. The effect of time and atmosphere (O_2, Air and N_2) of irradiation on the physico–chemical properties of wool has been studied. Data is also presented for wetting and dyeing properties of wool.

EXPERIMENTAL

Materials

Scoured woven wool fabric having plain weave (GSM-96, EPI-73, and PPI-66) was used for the study. It was scoured using 0.5 g/L Lisapol N (nonionic surfactant) at 80°C for 30 min with MLR of 1 : 40 and rinsed with hot water followed by cold water. It was then air dried and stored in a desiccator over P_2O_5.

Excimer UV radiation chamber

Xenon Excimer UV lamp (Xeradex 20W/L40/120/SBSX46/KF50) and the high voltage power supply (DBD 110V/230V 50 Hz/60 Hz) for the lamp were procured from Messrs Radium Lampenwerk Wipperfurth, Germany. The lamp emits almost monochromatic light in VUV region ($\lambda = 172$ nm) with the irradiation power of 50 mW/cm^2. The lamp was mounted in a chamber as shown in Figure 1.

Irradiation of the sample

The scoured wool fabric samples of size (10 cm × 2 cm) were irradiated for 1, 5, 10, and 15 min, under atmospheric pressure in Air, O_2, and N_2 atmosphere at a distance of 5 mm from the lamp.

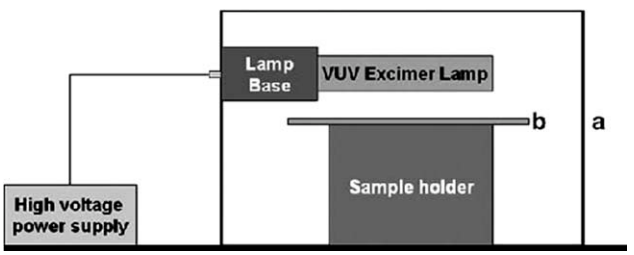

Figure 1 Schematic diagram of irradiation chamber (a) Stainless steel chamber (b) wool fabric.

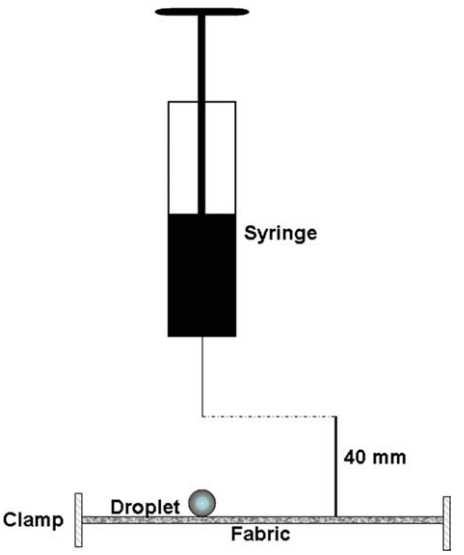

Figure 2 Schematic of the setup used for measuring the wetting time of the fabric. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Characterization studies

Treated wool samples were tested for change in performance properties such as wetting and dyeing behavior and for change in surface topography brought about by UV exposure. All samples were conditioned for 24 h in standard atmosphere before testing.

Wetting time was measured as the time taken for the absorption of a water droplet by the fabric. Fabric was held horizontally at its two ends, with clamps, keeping it free of folds. A drop of water was released onto it from a syringe from a height of 40 mm. Time taken for the complete absorption of drop by the fabric was recorded using a stop watch. This test was repeated on five different parts of the fabric and the average wetting time was calculated. Schematic for the procedure used is shown in Figure 2.

Changes in surface morphology of wool fiber surface were studied with the help of a high resolution (up to 3 nm) scanning electron microscope (ZEISS EVO50) using SE detector, 20 kv power and gold coating of 100 Angstroms. ATR analysis was carried out to study the change in molecular composition of wool on exposure to radiation. Perkin–Elmer 16PC FTIR spectrometer in ATR reflection mode with a zinc selenide crystal was used for the purpose.

Studies on dyeability of wool

Dyeing of wool with acid dye

Wool samples were dyed with Acid dye Navimill yellow 56N at 2% shade (on weight of fiber) at 60°C

TABLE I
Effect of atmosphere of irradiation on wettability of wool

Time of irradiation (min)	Wetting time (s)		
	Air	O_2	N_2
0	280	–	–
1	22.2	16.1	29
5	1.48	1.25	5
10	1.00	0.79	0.89
15	0.46	0.48	0.48

using material to liquor ratio of 1 : 40 for varying lengths of time in a shaking water bath. pH of the bath was maintained at 5 using 0.5 g/L of acetic acid.

Exhaustion of dye bath

Dye bath exhaustion was measured by sampling the concentration of dye bath before and after dyeing for 20, 30, 60, 90, and 120 min. Absorbance of the dye solution was measured using UV-Vis spectrophotometer (Perkin–Elmer, Lambda 25) at the 425 nm (λ_{max}). Extent of dye bath exhaustion (% E) was calculated using the following equation:

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

where A_0 is the absorbance of dye solution before dyeing and A_t is the absorbance of dye solution after dyeing for t minutes.

Shade depth of dyed fabric

After dyeing, the shade depth in terms of K/S values of dyed wool samples was measured with Gretag Macbeth computer color matching instrument using D65 light source and 10° observer. K/S are values calculated from reflectance data according to the Kubelka–Munk equation given below:

$$K/S = (1 - R)^2/2R \quad (2)$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the dyed fabric at the wavelength of maximum absorption.

RESULTS AND DISCUSSION

Wool fabrics were exposed to 172 nm UV excimer lamp in air, O_2 and N_2 atmosphere. Effect of irradiation on the performance properties such as wetting, dyeability, surface chemistry, and surface morphology of wool has been studied. Results of the studies are reported later.

Wettability of wool

Wettability of a surface can be defined as the time taken for a drop of water to be completely absorbed by a fabric and it depends on the hydrophilicity of the surface being wetted. Wool as a fiber is characterized by a hydrophilic core protected by an outer surface rendered hydrophobic by the presence of a thin (0.9 nm) layer of fatty acids on its epicuticular surface.[9] This layer does not get removed even during the scouring of wool and the fiber continues to be hydrophobic on the surface thus making it difficult to dye and process it using aqueous industrial processes.

Table I shows the results of wettability of wool when exposed to 172 nm UV radiation in air, oxygen or nitrogen atmosphere. Irradiation reduces the wetting time of wool nearly by a factor of 10, even after an exposure of 1 minute, irrespective of the atmosphere used. The effect of UV exposure is immediate. Wetting time continues to decrease with increasing time of exposure. At 15 min of exposure, the absorption becomes instant, thus indicating that fiber surface is highly hydrophilic.

Several physical and chemical reactions are responsible for the observed hydrophilicity of wool after UV exposure. The first phenomenon is commonly known as the ozone–oxygen cycle.[9] Oxygen from the atmosphere absorbs high-energy photons from the excimer to form highly reactive excited oxygen O (1D) either directly or first forming O_3 (ozone) and then dissociating into O (1D) and O_2. The presence of nitrogen in air plays an important role in the production of such reactive excited oxygen species.[10,11] The excited oxygen O (1D) in turn oxidizes the fatty layer and reacts with the fiber surface to form oxygen containing polar groups such as hydroxyl (—OH) and carbonyl (—C=O).[12]

However, by far the most important oxidation reaction is the oxidation of disulphide protein linkages (—S—S—) to give S^{VI} in the form of anionic sulphonic acid groups (—SO_3H)[9,13] accompanied by intermediate products like cystine monoxide and cystine dioxide.[13] Amount of S^{VI} on wool surface has been shown to have a linear relationship with its wetting behavior.[3,9] In Table I also samples treated in O_2 atmosphere show the least wetting time upto 10 min of exposure. Creation of these reactive sites makes the fiber hydrophilic and more receptive to dyes and chemicals particularly those carrying reactive nucleophilic groups.[14] Surface functionalization by creation of oxygen rich groups coupled with the destruction of the fatty barrier layer of wool makes the fiber surface hydrophilic on exposure to UV radiation.

In N_2 atmosphere, the increase in hydrophilicity is due to the severe etching of the surface and also the

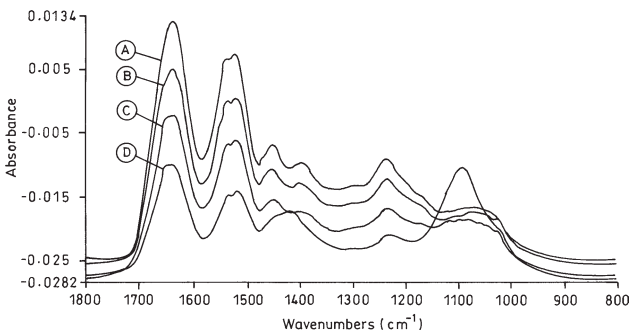

Figure 3 ATR spectra of UV treated wool in different atmospheres (A) Control (B) O_2 (C) N_2 and (D) Air.

creation of NH_2 groups.[15] This effect has been discussed later with respect to the dyeing studies.

ATR analysis

Treated and untreated wool samples were subjected to ATR analysis with a view to confirm the presence of functional groups mentioned above. ATR investigations provide information about the chemical nature of the outer 10^{-6} m of modified fiber surfaces. However, no significant change is observed in the spectra of samples treated with UV, Figure 3. The strongest peaks in all spectra occur at around 1627 cm^{-1} and 1511 cm^{-1} and are attributable to primary and secondary amide (—CONH). Absorbance around 1000–1450 cm^{-1} indicates sulphur-oxygen band of sulphonic acid.[9,15]

Physical changes in the surface of wool

SEM micrographs of the untreated and UV treated wool fabric in air, O_2 and N_2 atmosphere are shown in Figure 4. The sharp, well defined contour of scales seen in the untreated wool sample (A) seem to have smoothened out significantly on irradiation in all atmospheres and the surface of treated fibers appear to be less waxy. Surface topography of samples treated in nitrogen atmosphere (D) appears to be significantly different from the other samples. The typical scale geometry of wool is not visible and there are deep striations on the surface. The fiber surface appears to have been etched and roughened by irradiation. Reason for this typical appearance is unknown at this stage. Micropores can be seen on the sample exposed in O_2 atmosphere. The samples thus seem to have undergone ablation and etching due to UV exposure but this change in surface morphology has only a minimal effect on the wetting behavior. Increase in surface hydrophilic groups along with surface roughening may significantly

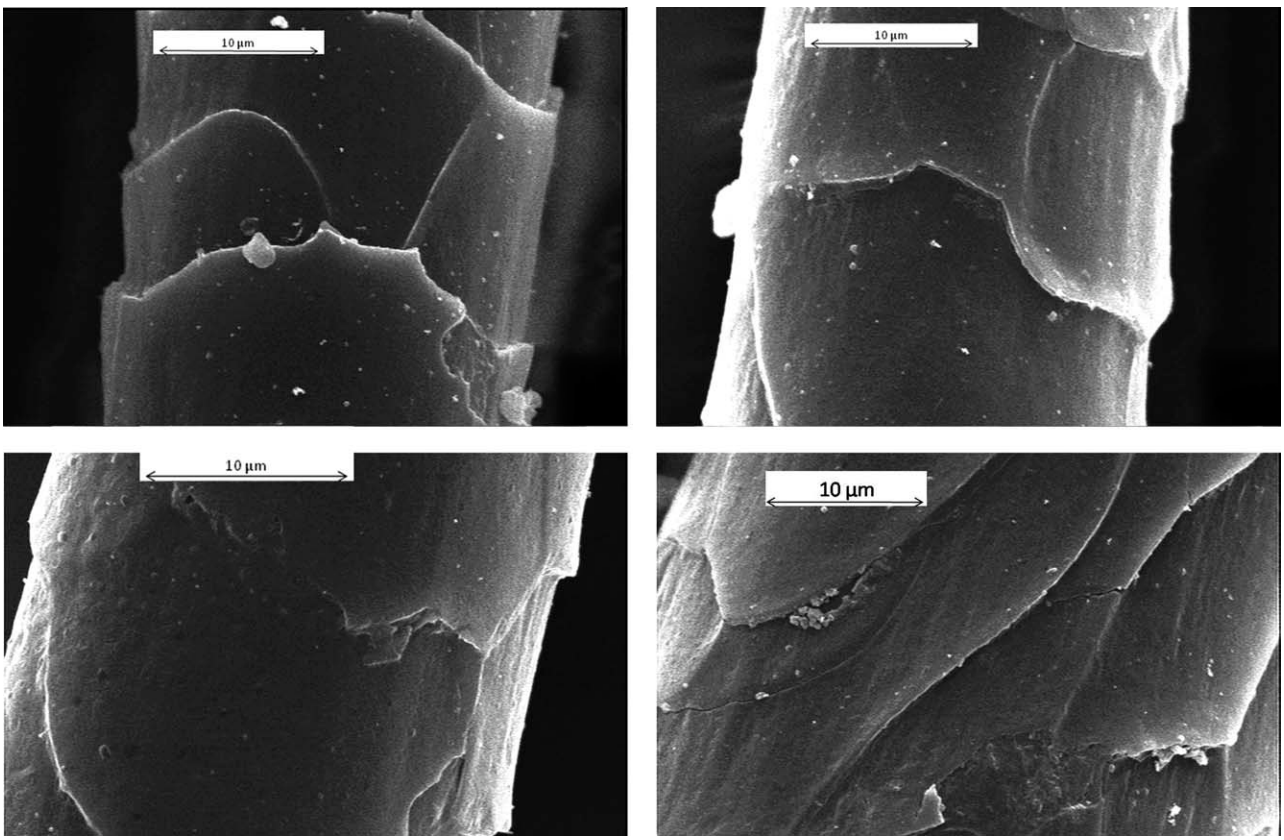

Figure 4 SEM micrographs (x3000) of wool fibre exposed to UV Excimer lamp for 15 min. (A) Control (B) Air (C) O_2 and (D) N_2 atmosphere.

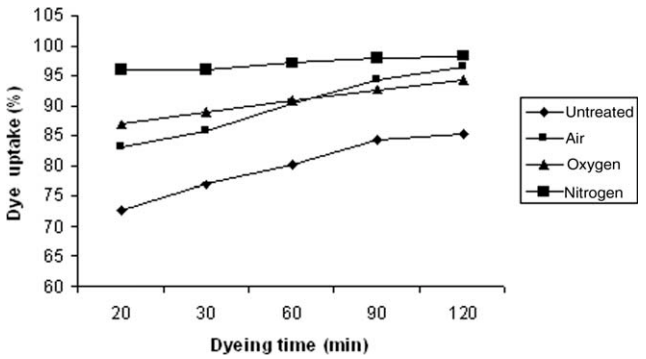

Figure 5 Uptake of Acid dye by wool treated with UV radiation for 15 min.

contribute to the adhesive forces between the fiber surface and water molecules leading to improved dyeability. Wool fibers thus prepared can be expected to show better dyeability as well as better adhesion for coatings and finishes.

Dyeability of wool

As wettability of wool is seen to increase appreciably on irradiation, it is expected that its dyeing behavior would also be modified. Anionic acid dye Navilan yellow 56N was used to dye the wool samples irradiated for different time periods in air, O_2 and N_2 atmosphere. Exhaustion of dye bath and the color value of the dyed fabric were used to evaluate the dyeability of fibers. Results for rate of dye uptake at 60°C for untreated sample and samples treated with UV for 15 min in different atmospheres are shown in Figure 5.

All treated samples show higher uptake of dye at the end of dye cycle as compared to untreated one. The rate of dye uptake is also significantly higher for all treated samples as seen by the amount of dye taken up after various intervals of dyeing. Nearly 100% dye is exhausted within 20 min of dyeing for sample treated in N_2 atmosphere as compared to 73% for untreated wool. Samples treated in air and O_2 atmosphere show an identical trend. However, samples treated in nitrogen exhibit much higher dyeability. At exhaustion too, 100% of the dye is exhausted in nitrogen treated sample as compared to 84 and 93% for untreated sample and samples treated in air and oxygen atmosphere respectively.

Change in color strength value (K/S) of dyed fabric as a function of exposure time is shown in Table II. There is a direct relation between the length of exposure to UV and the amount as well as the rate at which the color depth increases on fabric. Maximum depth is observed for samples treated in N_2 atmosphere.

Improved dye uptake by all treated samples can be attributed to the destruction of the lipid barrier layer and decrease in the number of disulphide groups (S—S) in the keratin that act as a barrier to the diffusion of aqueous solutions. Enhanced uptake of dye by samples treated in N_2 atmosphere can be attributed to the creation of additional —NH_2 groups on the fiber which provide cationic sites for the attachment of acid dye in acidic pH.[16–18] This can be a very critical finding in dyeing and finishing of wool where irradiation could be used to shorten the dye cycles or reduce the temperature of dyeing, while at the same time reducing the consumption as well as wastage of dyes. All these benefits come without any loss of fabric strength or fabric handle (common in chemical treatments) as the changes are restricted to nano meter level at the fiber surface.

CONCLUSION

Monochromatic UV irradiation of 172 nm can modify the surface properties of wool to an appreciable extent. 15 min of exposure time brings about notable changes in the surface morphology as well as surface chemistry of wool as seen by the SEM analysis and the improved wetting and dyeing behavior of all treated samples. Most dramatic effects are observed for treatment in N_2 atmosphere for 15 min. SEM of these samples shows deep striations on the surface and the scale structure is greatly modified. It

TABLE II
K/S value of wool fabrics treated with UV and dyed with Acid dye

Time of irradiation	Dyeing time (min)	*K/S*		
		Atmosphere		
		Air	O_2	N_2
0 min				
	20	7.453		
	30	7.878		
	60	8.744		
	90	8.750		
	120	9.011		
1 min				
	20	7.89	7.82	7.47
	30	9.02	9.21	9.50
	60	9.98	9.50	10.08
	90	10.43	10.34	10.25
	120	13.46	10.95	12.27
5 min				
	20	10.23	10.70	12.38
	30	10.62	11.52	13.26
	60	11.55	11.92	13.68
	90	12.71	12.18	13.81
	120	13.55	12.55	14.93
15 min				
	20	11.12	11.27	13.38
	30	11.21	11.77	15.40
	60	12.35	12.14	16.19
	90	12.83	12.34	16.62
	120	14.02	12.77	17.06

possibly leads to creation of additional amino groups as corroborated by increased uptake of anionic dyes for these samples. It may hence be concluded that UV radiation has the potential to be exploited in design and development of cleaner, more effective and more efficient commercial processes for dyeing and finishing of wool.

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