

A Study on Xe₂* Excilamp Treatment of Wool Fibers

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ABSTRACT: A Xe₂* excilamp ($\lambda = 172$ nm) was applied to photo irradiate and surface modify wool fibers. The scanning electron microscopy (SEM) showed that the outer surface of the fibers was etched after excilamp treatment, and some microcracks emerged on the surface scales. X-ray photoelectron spectroscopy (XPS) analysis indicated that the excilamp-treated fibers possessed high concentration of oxygen, sulfur, and nitrogen, as well as increased hydrophilic groups, such as hydroxyl group, carboxyl group, and sulphur oxide species on the surface. Fourier transform infrared spectroscopy with attenuated total internal reflectance (FTIR-ATR) mode measurement showed that the sulphur oxide species was mainly composed of

cystic acid and S-sulphonate together with a small amount of cystine monoxide and cystine dioxide on the outer surface of excilamp-treated wool fiber. The contact angle of water on the excilamp-treated fiber decreased about 110°. Using an acid dye, deeper hue was achieved in dyeing the treated fibers, evidenced by improved relative color strength (K/S) and brightness (L^*) values. And the directional friction effect (DFE) of the wool fibers in wet obviously decreased after the excilamp treatment. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 241–246, 2010

Key words: wool fibers; Xe₂* excilamp; surface morphology; hydrophilic groups

INTRODUCTION

The outer surface of wool fiber, the cuticle cells, are hydrophobic in nature due to the presence of proteins in high cystine-disulphide content along with covalently bound fatty acids, acting as a surface barrier against diffusion and penetration of dyestuffs and finishing agents into the wool-structure.^{1,2} And it is the cuticle or scale cell structure of wool fiber that is primarily responsible for felting by fiber entanglement, causing a corresponding shrinkage of wool fabrics, most particularly in laundering. Apart from dyeing, shrink-proofing process is the most common treatment applied to wool. Therefore, there is a requirement for research on promoting ecologically acceptable and environmentally sustainable wool surface modification technology for shrink-proofing, dyeing, and finishing.^{3,4}

Excilamps, one kind of novel powerful and effective photo-irradiation source, has already been used in water and air purification, biomedical application, and semiconducting material deposition because of its ecological, economical, and operational characteristics. However, there has been only a few studies on using excilamps in surface modification of textile materials, and no report on treatment of wool fiber so far.^{5,6}

In this work, a Xe₂* excilamp was applied to the surface modification of wool fibers. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy with attenuated total internal reflectance (FTIR-ATR) analyses were used to investigate the impact of excilamp treatment on surface morphology and chemical composition of the fibers. The contact angle and directional fraction effect (DFE) were also measured before and after the excilamp treatment to assess the improvement of the surface wettability and shrink-proofing property. Color depth was evaluated to study the dyeing properties of the treated fibers.

EXPERIMENTAL

Materials

Greige wool twills provided by Shandong Ruyi Wool Mill Company were scoured with 4 g/L soap

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solution at pH 9 (adjusted with sodium bicarbonate) in a liquor ratio of 10 : 1 at 45°C, followed by cleaning in distilled water and air drying.

An acid dye, Optilan MF-3B 140 (C.I. Acid Red 131), was obtained from Clariant Company (China) and used as received.

Excilamp treatment of wool samples

The excilamp treatment of wool samples was conducted on a Xe₂ excilamp, with a model Bluelight Compact 172/120Z, manufactured by Heraeus-Noblelight, Germany. It emits quasi-continuously with a center wavelength of 172 nm, a spectral bandwidth of about 16 nm, and an intensity of about 50 mW/cm². The Xe₂ excilamp consists of a tube filling with high-pressure Xenon gas and a power supply with 20 W output. In this study, the samples were irradiated under the lamps at a distance of 0.5 cm for 0.5 min, 1 min, 2 min, 5 min, and 8 min, respectively.

Surface analyses

SEM (JSM-5600LV type, Japan) was used to analyze the surface morphology of control as well as treated wool fibers. The magnification of the images was set at 5,000×. Before the SEM experiment, the fiber was coated with a vapor-deposited thin layer of gold to induce conductivity.

The analysis of surface chemical compositions was evaluated by using an ESCALAB 250- Multitechnique surface analysis system (XPS) (Thermo Fisher Scientific Inc.) equipped with a single Al K α X-ray source (150 W). The C1s and S2p core level spectra were recorded to determine the surface composition changes.

The infrared spectrum of the excilamp-treated wool fibers was determined by means of Nicolet Nexus 670 FTIR spectrometer in ATR reflection mode using a Ge crystal (Nicolet, USA). The areas of every relevant signal between 1000 and 1200 cm⁻¹ wavenumber in spectrum were measured and calculated with PeakFit software.

Wettability: Contact angle measurements

Contact angle measurements were performed for quantifying wettability of fabrics. They were measured using the sessile drop method with a JY-82 Contact Angle tester (Hebei Chengde tester Co., China). Distilled water was used as the test liquid, and was dropped onto more than ten different locations on the fabric surface at 20°C, RH 65%.

Dyeing evaluation: Relative color strength (K/S) and brightness (L*)

The dyeing process was carried out in a Rapid H-12F dyeing machine (Rapid Labortex Co. Ltd.). The dye liquor for 0.5% depth of dyeing (o.w.f.) was composed of 1 g/L sodium acetate and 5 g/L sodium sulfate at a liquor ratio of 15 : 1. And the pH was adjusted to 4.5 by acetic acid. After the addition of the auxiliaries and samples the dye-baths were heated from 40 to 98°C at a rate of 1°C/min and maintained for 45 min.

For evaluation of the color depth of the dyed samples, the relative color strength (K/S) and brightness (L*) values were measured by the Datacolor-SF600 Spectrophotometer under illuminant D₆₅, using a 10° standard observer.

Shrink-proofing property: Fiber-to-rubber friction measurement

Shrink-proofing property was assessed via the directional friction effect (DFE). Wet friction coefficients of the fiber (to rubber) in with-scale direction (μ_w) and against-scale direction (μ_a) were measured using winch method with a fiber coefficient tester (Changzhou, China) in both static and kinetic states, respectively. The DFE was the difference between the μ_a and μ_w values.

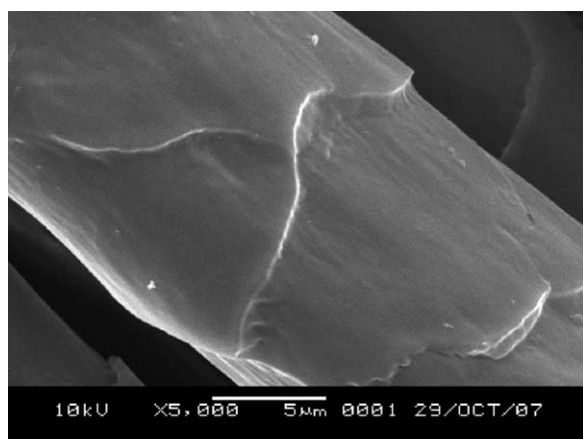
RESULTS AND DISCUSSION

Morphological analysis by SEM

The surface morphology of wool fibers treated under the Xe₂ excilamp irradiation revealed a significant change, which is illustrated by SEM images in Figure 1. The control wool fiber presented a relatively smooth topography on the fiber surface [Fig. 1(a)]. By contrast, the fiber after the excilamp-treatment for 8 min displayed rougher surfaces. It was clear in the images that some continuous microcracks emerged parallel in the direction of the fiber axis on the surface scales of the wool fiber [Fig. 1(b)]. As the active species of the excilamp were mainly UV photons and there was no significant temperature rise on the samples surface, the surface etching with incoherent UV radiation originating from excilamp is mainly of photolytic nature.⁷

Chemical composition analysis by XPS

XPS technique was applied to analyze the chemical structures in the outermost (5–10 nm) layer of the wool fibers. The element composition of control and treated samples are given in Table I. When compared with the control, the elemental percentages of oxygen, nitrogen, and sulfur of fiber surface after



(a)



(b)

Figure 1 SEM images of the wool fibers: (a) control and (b) excilamp-treated, 8 min.

Xe₂^{*} excilamp treatment for 8 min were dramatically raised by 155%, 63%, and 343%, respectively, at the expense of the carbon atomic percentage. This chemical composition change for the treated sample could be a result of photo-oxidation by introducing oxygen into the surface of fiber. And severe etching by the excilamp would be another reason which removed the outer surface and thus made the protein material located beneath it directly exposed at the surface with more sulfur and nitrogen atomic percentage.⁸

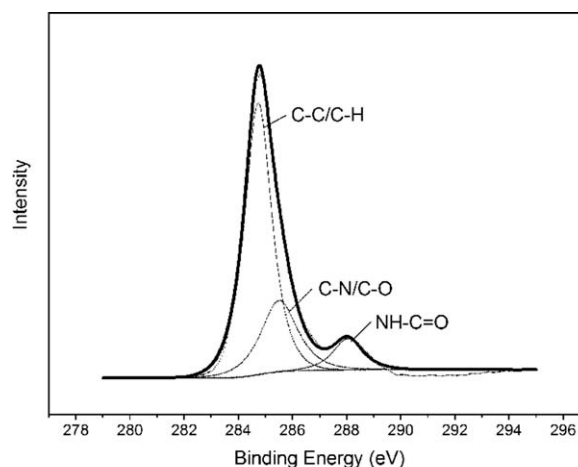
The deconvolution analyses of C1s peaks are performed as expressed in Figure 2. The C1s spectrum of control specimen is fitted to three parts: a major

TABLE I
XPS Elemental Analysis of Control and Treated Wool Fibers

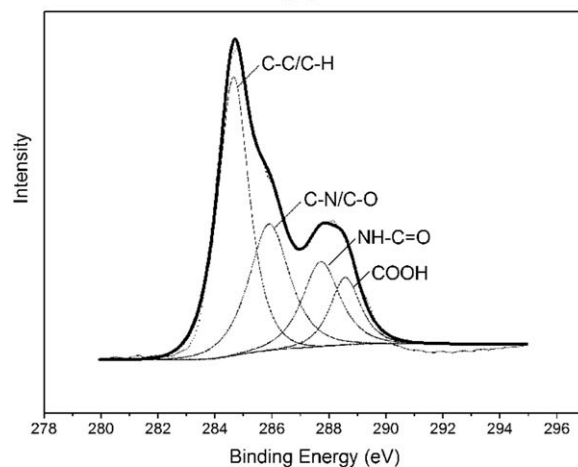
Sample	Chemical composition (%)				
	C1s	O1s	N1s	S2p	Others
Control	78.96	13.88	4.57	1.02	1.57
Xe ₂ [*] excilamp treated for 8 min	50.59	35.38	7.44	4.52	2.07

peak at ~ 285 eV attributed to aliphatic carbon atoms, a peak at 286.4 eV corresponding to the carbon atoms in C–N/C–O bonds and a peak at 288.3 eV arising from the carbon atoms in amide group (–CONH–). After the excilamp treatment for 8 min, it can be seen that the newly oxidized carbon functional group, carboxyl group (O–C=O, 289.4 eV) is imparted to the fiber surface, at meantime, the intensity of carbon atom in C–N/C–O bonds and amide group increased with the decrease of aliphatic carbon atom.^{9,10} The quantitative evaluations of the changes (Table II) confirm that carbon-oxygen groups attributed to C–O, C=O and O–C=O functionalities are formed due to the excilamp photo-oxidation.

The deconvolution analysis of S2p is shown in Figure 3. The S2p peak of the control arising from the disulphide bonds (S–S) is at ~ 164 eV. After the excilamp treatment for 8 min, the S2p spectrum shows that the main peak shifts to ~ 168 eV corresponding to the cystine oxidation products (–SO_x).¹¹



(a)



(b)

Figure 2 Deconvoluted XPS C1s spectra for wool fibers: (a) control and (b) excilamp-treated, 8 min.

TABLE II
Data of Deconvolution of C1s, and S2p peaks for Control and Treated Wool Fibers

	Sample	Sample		
		Control	Xe ₂ * Excilamp treated for 8 min	
Relative area corresponding to different chemical bonds (%)	C1s	C—C/C—H	67.68	45.57
		C—O/C—N	23.87	27.15
		—CONH—	8.45	16.60
		O—C=O	≤0.01	10.68
	S2p	S—S	100	4.20
		—SO _x	≤0.01	95.80

The data of deconvolution of S2p peaks given in Table II indicate that most of the disulphide bonds in the outmost of layer of wool fiber are cleaved during this photo-oxidation, which resulting the formation of —SO_x.

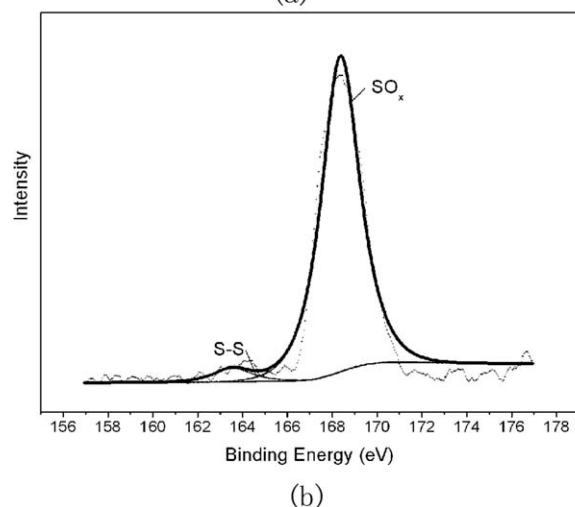
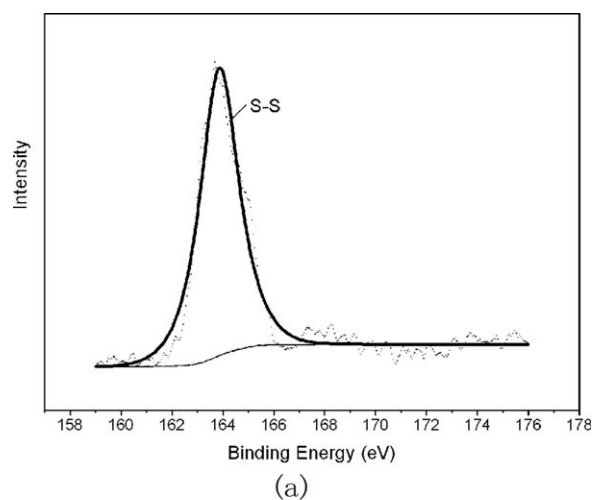


Figure 3 Deconvoluted XPS S2p spectra for wool fibers: (a) control and (b) excilamp-treated, 8 min.

TABLE III
Data of Deconvolution of S—O Vibration Region Peaks for Treated Wool Fibers

Species	Relative area (%)
Cystine dioxide (—SO ₂ —S—, 1121 cm ⁻¹)	9.51
Cystine monoxide (—SO—S—, 1071 cm ⁻¹)	6.87
Cysteic acid (—SO ₃ ⁻ , 1040 cm ⁻¹)	59.36
S-sulphonate (—S—SO ₃ ⁻ , 1022 cm ⁻¹)	24.26

Chemical composition analysis by FTIR-ATR

FTIR-ATR technique can provide qualitative and quantitative information of material surface. The penetration depth of FTIR-ATR into wool keratin has been estimated to be about 0.3–1 μm at 1200 cm⁻¹ depending on the nature of the particular internal reflective crystal used.¹² FTIR-ATR was explored here for a detailed analysis of cystine oxidation products induced by excilamp-treatment. The Peak-Fit software was used to fit peaks of the spectrum in S—O vibrational region (1000–1200 cm⁻¹) and measure the relative areas corresponding to different species (Table III).^{13,14} Table III shows that the main components of cystine oxidation products are cysteic acid and S-sulphonate, which account for 59.36% and 24.26%, respectively. The intermediate oxidation products, cystine monoxide and cystine dioxide, are also present in the surface of wool fibers, within the detected depth of FTIR-ATR.

Wettability

As shown in Figure 4, with increasing Xe₂* excilamp exposure time the contact angles of the treated samples reduced significantly, after the excilamp treatment for 8 min it decreased from 129.4° (partial non-wetting condition) to 19.9° (partial wetting condition) compared with the untreated sample.¹⁵ It

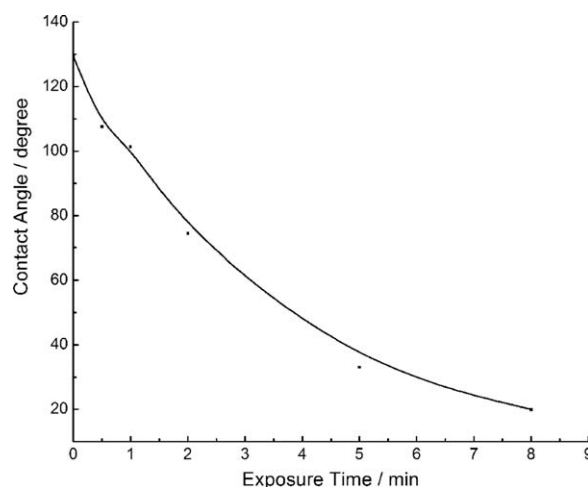


Figure 4 Contact Angles of the Wool fabrics after excilamp treatment.

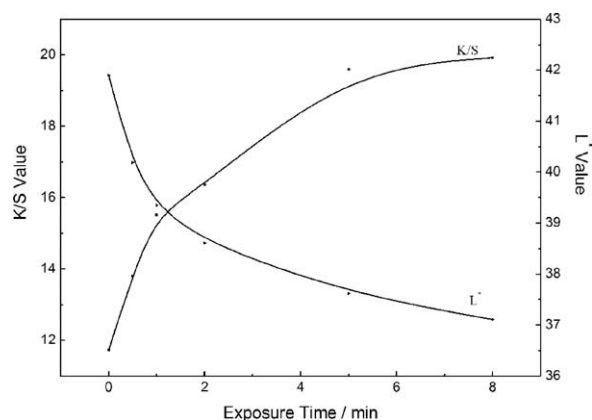


Figure 5 K/S and L^* values of the dyed samples with excilamp treatment.

indicates that the treatment could improve the wettability of the wool fibers, significantly.

In combination with the morphological and chemical composition analyses of wool fibers surface, the dramatic improvement in wettability of the treated specimens is the result of partial destruction of the epicuticle due to excilamp etching, reduction in the content of the covalently bond fatty acids and introduction of polar carbon-oxygen groups due to photo-oxidation, along with the conversion of cystine residues to sulfonic groups.^{2,16,17}

Dyeing studies (improvement of coloration)

The relative color strength (K/S) and brightness (L^*) values of the dyed specimens with Xe₂* excilamp treatment are shown in Figure 5. With increasing excilamp exposure time the K/S values of the dyed samples increased, from 11.728 of the control sample to 19.925 of the exposed for 8 min, while the L^* values decreased from 41.90 to 37.11. Therefore, the excilamp treatment improved dyeability of wool fibers significantly and provided deeper hue effect, which will be good at the development of new wool products through novel coloration effects.⁴

Combining with the results of surface analyses, the effect of the deeper hue is mainly caused by the scattered reflection on the rougher surface of the excilamp-eroded wool fibers. In addition, the conversion of disulphide bonds to sulfonic groups might improve diffusion of dye molecules through altering the hydrophilic character of the fiber surface.

Shrink-proofing property: DFE assessment

The shrinking properties of woolen textiles (a.k.a. felting) in the presence of water and mechanical agitation are due to the occurrence of scales at the wool

fiber surface. Both kinetic and static effects are involved. Kinetically, the most important physical property is the difference in frictional coefficients in the against-scale and with-scale directions, i.e., DFE. Statically, the hydrophilic character of the fiber surface is most important.¹⁸

Figure 6 presents the columns of frictional coefficient of control and excilamp-treated fibers both with the scales and against the scales in static state and in kinetic state, respectively, the DFE values are also shown in it. The results indicate that after excilamp treatment for 8 min the values of the friction coefficient with the scales of the fiber increased more than that against the scales in comparison with that of the control fiber not only in static state but in kinetic state, in consequence, the values of the DFE of the excilamp-treated sample were less than that of the control one. It may be resulted from the rougher surface of the treated fibers that induced reduction in movement and entanglement of scales. Therefore, excilamp treatment will be a novel shrink-proofing process as it alters the hydrophilic character of the fiber surface and reduces the DFE of fiber.

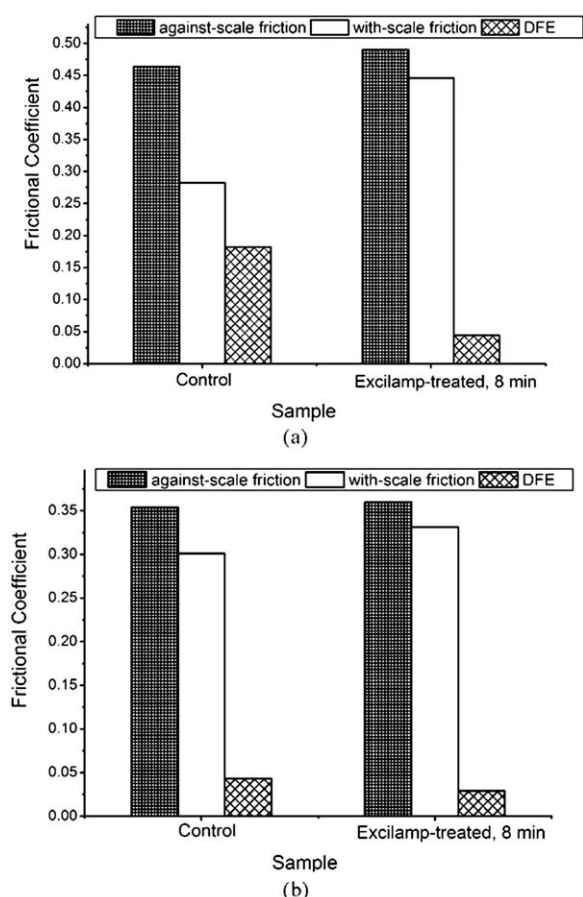


Figure 6 Effect of excilamp treatment on frictional coefficient and DFE in (a) static state and (b) kinetic state.

CONCLUSIONS

Excilamp treatment is a novel and environmentally friendly process that can be applied to surface modification of wool fibers. In this article, with SEM analysis it was confirmed that the treatment increased roughness and appearance of some micro-cracks of wool fibers. The results of the XPS indicated that treated fibers had higher concentration of oxygen, sulfur and nitrogen, more polar carbon-oxygen groups, such as, C—O, C=O and O—C=O, along with conversion of disulphide bonds to sulfonic groups than the control fiber. FTIR-ATR measurement suggested that after excilamp treated for 8 min, about 60 percent of cysteic acid was formed as a result of the cleavage of disulphide linkage together with some intermediate oxidation products of cystine on the surface. Compared with the control fiber, the contact angle of the excilamp-treated fiber decreased from 129.4° to 19.9°. And the relative color strength (K/S) and brightness (L^*) values showed that the excilamp treatment provided the dyed wool fibers with deeper hue effect. And the directional friction effect (DFE) of the wool fibers in wet did obviously reduce after excilamp treatment. Therefore, excilamp treatment improved the wettability, color depth, and shrink-proofing properties of the wool fibers.

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