Comparative Study of the Structure and Properties of Wool Treated by a Chicken-Feather Keratin Agent, Plasma, and Their Combination

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Received 17 February 2010; accepted 21 May 2010
DOI 10.1002/app.32853
Published online 19 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Wool was treated by a chicken-feather keratin agent, plasma, and their combination. These treated wools were characterized with Fourier transform infrared spectroscopy and scanning electron microscopy. The performance properties, such as the antifelting performance, wettability, and dyeability, of these treated fibers were tested. The results show that the antifelting performance, wettability, and dyeability of the wool modified by plasma combined with the chicken-feather keratin were improved. This joint treatment technology is an environmentally friendly green ecological finishing technique. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1627–1634, 2011

Key words: dyes/pigments; fibers; modification; structure–property relations; waste

INTRODUCTION

Protein molecules containing many hydrophilic polar groups, such as amino groups and carboxyl groups etc, have a high hydrophilicity and good affinity to skin, so they can be used as caring, natural, value-added finishing agents for fabrics.

Protein materials are present worldwide, such as in sericin, a variety of discarded animal hairs, and chicken feathers. However, many kinds of protein materials are discarded as a trash and are not used fully. If waste protein could be used as a valuable resource, it could not only turn waste to treasure but also reduce environmental pollution. There is growing interest in the recovery of waste protein, which has founded effective applications in the areas of cosmetics, food, medicine, and textiles.[1–7]

Recently, many studies concerning reused waste protein material have focused on the use of sericin to overcome polyester hydrophobicity and to improve the UV-absorption properties of sericin-treated fabrics[8,9] and the antifelting of sericin-treated cashmere hair.[10] However, studies with regard to the chicken-feather keratin used on wool to improve its antifelting and dyeing abilities have rarely been reported. The aim of this study was to develop various application areas in the field of textiles for chicken-feather keratin, to decrease pollution, and to use the waste effectively.

Wool is easy to felt; traditional antifelting methods exist for the absorbable halogen compound, which is one of the sources of absorbable organic halogens. Also, the traditional dyeing of wool is done at 98°C, which causes a bigger consumption of energy and more damage to the fiber. This does not fall well with the requests of people for environmental protection.[11,12] The technology of plasma, as a dry process, is praised for being a "green" technology, which is enormously important to people. Researches have shown that plasma treatment alone can improve the antifelting properties of wool, but it cannot reach the requirement of being machine washable, so subsequent processing is necessary after the plasma treatment.[13–17]

In a previously study, we studied the preparation of a keratin solution from chicken feathers and its influence on the felting ability of wool and optimized the preparation conditions of the chicken-feather keratin agent and the modification conditions of wool by plasma combined with the chicken-feather keratin agent.[18,19] In this study, the prepared chicken-feather keratin agent was characterized with Fourier transform infrared (FTIR) spectroscopy. Wool was treated by the chicken-feather keratin agent, plasma, and their combination, respectively. The structure and performance properties (antifelting properties, wetting time, and dyeing behavior at low temperature) of the treated fiber was studied and is discussed.

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Contract grant sponsor: Education Department of Shannxi Province; contract grant number: 05JK203.

EXPERIMENTAL

Materials and instruments

Wool top was supplied by Beijing Ailide New Textile Products Co., Ltd. (Beijing, China). Pingpingjia O, a nonionic surfactant, was provided from Tianjing Tianzhu Fine Chemical Co. (Tianjin, China). Chicken-feather keratin was collected from a slaughterhouse (Xi'an, China). Dyeing involved three dyes, Lanasol Red 6G (C.I. Reactive Red 84), Lanaset Red G, and Lanaset Blue 3G (the Lanaset range was composed of a modified 1 : 2 metal complex and acid and reactive dyes with high wetting and lightfastness), which were produced by Ciba Co., Ltd. (Panyu, China). All other reagents were analytical grade and were purchased from Xi'an Chemical Reagent Co., Ltd. (Xi'an, China). We made the plasma equipment used in this experiment.[20] The FTIR-5700 infrared spectrogram instrument was made by Thermo Nicolet Corp. (Madison, WI). The KYKY-2800 scanning electron microscope was provided by China Science Academe Beijing Science Instrument Co., Ltd. (Beijing, China). The HD500-type dyeing apparatus and a laboratory water bath oscillator were provided by Nantong Experimental Instrument Co. (Nantong, China). The 722 type spectrophotometer was provided by Shanghai Third Analytical Instrument Factory (Shanghai, China). The SW-12A type laboratory laundering machine, which was used for the felt-ball density test and washing-fastness test, was provided by Wuxi Textile Instrument Factory (Wuxi, China). The SF-300 SRICI computer, used to measure and match colors, which was used in the dye depth and dye brightness tests, was provided by SRICI Color Science and Technology Co., Ltd. (Shenyang, China).

Processing treatments

The wool top was cleaned with an aqueous solution of a nonionic surfactant (Pingpingjia O: 2 g/L), rinsed with water, and allowed to dry in air. The cleaned wool top was treated by plasma or/and treated with chicken-feather keratin agent.

Wool-top treatment with plasma

The glow-discharge generator used for the treatments was a radio-frequency etching system operating at 13.56 MHz. Air plasma was used to treat the wool top in an experiment in which the sample was placed in the chamber with the air entering valve shut while the vacuum was drawn up to a pressure of 50 Pa; the discharge was carried out at 150 W for 5 min. Then, the air valve was opened so that the system pressure returned to normal, and the treated fiber was removed from the reactor.

Preparation of the chicken-feather keratin agent[18]

Chicken feathers were collected from a slaughterhouse. Then, the collected chicken feathers were cleared and dissolved with a solution containing 7.5 g/L NaOH and 8 g/L urea at 85°C for 2.5 h; the ratio of solid to liquid was 1 : 20. Finally, the dissolved keratin solution was neutralized with hydrochloric acid until its pH was neutral. The chicken-feather keratin agent was obtained and readied for application.

Wool-top treatment with the chicken-feather keratin agent[19]

The concentration of chicken-feather keratin agent was 14 g/L (material-to-liquor ratio = 1 : 50); the wool was treated at 80°C for 50 min, then dried at 100°C for 3 min, and baked at 110°C for 3 min.

Dyeing technology

The different treated wool tops were dyed in an HD500 type dyeing apparatus with 2% on the mass of the fiber Lanaset Red G, Lanaset Blue 3G, or Lanasol Red 6G with a liquor ratio of 1 : 40. Then, 2 mL/L acetic acid was added to the dyeing bath. The dyeing process commenced at 50°C, and then, the temperature of the dyeing bath was raised to 85°C at a rate of 1°C/min. Dyeing was carried out at this temperature for 30 min.

Measurement of the targets

Measurement of the infrared spectrogram

The FTIR spectra of the chicken-feather keratin agent modified and unmodified wool tops were recorded on the FTIR-5700 infrared spectrogram instrument with the KBr pellet technique. We prepared the KBr pellets by grinding 1 part of the sample with 9 parts of spectral-grade KBr and pressing them in an evacuated die under a suitable pressure to obtain pellets.

Measurement of the scanning electron microscope

After the samples were coated with gold *in vacuo*, the surface morphological structures of the modified and unmodified wool tops were measured with the KYKY-2800 scanning electron microscope.

Test of the wool felt-ball density

The wool (1 g) was placed in the SW-12 A type wash test machine along with a nonionic surfactant (Pingping Jia O, 3% on the mass of the fiber) at 45°C for 30 min at a liquor ratio of 1 : 40, and six steel balls were added to the container. Afterward, the wool was removed from the containers, rinsed twice

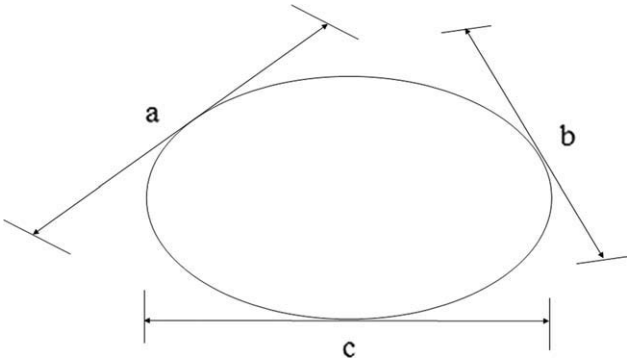

Figure 1 Measurement of felted ball diameter.

with cold water, placed in an oven at 105°C for 2 h, and then conditioned for 24 h before measurement. A caliper was used to measure the average diameter of each felted ball, as shown in Figure 1. In each direction (a, b, and c, as shown in Fig. 1), four readings were collected and averaged. The felt-ball density (ρ; g/cm^3) of each ball was calculated according to the following equation:[13]

$$\rho = \frac{m}{v} = \frac{6m}{\pi d^3} = \frac{m}{0.524d^3} \quad (1)$$

where m is mass of the cashmere fiber, v is volume of the cashmere fiber, and d is the average diameter.

The smaller the felt-ball density was, the better the antifelting performance of the wool was.

Measurement of the wettability

One drop of distilled water was dropped on the leveled wool top, and the wetting time of water (in seconds) was measured after the water drop completely penetrated the flat wool top from a height of 3 cm. Four readings were collected and averaged. The smaller the penetrating time was, the better the wettability was.

Measurement of the dye uptake

The absorbance of the dye liquor was measured with the 722 spectrophotometer before and after dyeing, respectively. Then, the dye uptake was calculated according to the following equation:

$$E(\%) = \left(1 - \frac{nA_i}{mA_o}\right) \times 100\% \quad (2)$$

where E is the dye uptake, A_i is the absorbance of the dye liquor after dyeing and n times dilution, and A_0 is the absorbance of the dye liquor before dyeing and m times dilution.

Measurement of the dye depth

The dye depth of the flat wool top was measured with the SF-300 SRICI computer spectrophotometer, which measured and matched colors. The measurement was carried out under the illuminant D_{65} and with a 10° observer at the maximum wavelength. The bigger the dye depth values were, the deeper the dyed fiber was.

RESULTS AND DISCUSSION

Infrared spectrogram of the chicken-feather keratin agent

The IR spectrum of the chicken-feather keratin agent, presented in Figure 2, showed that there was an

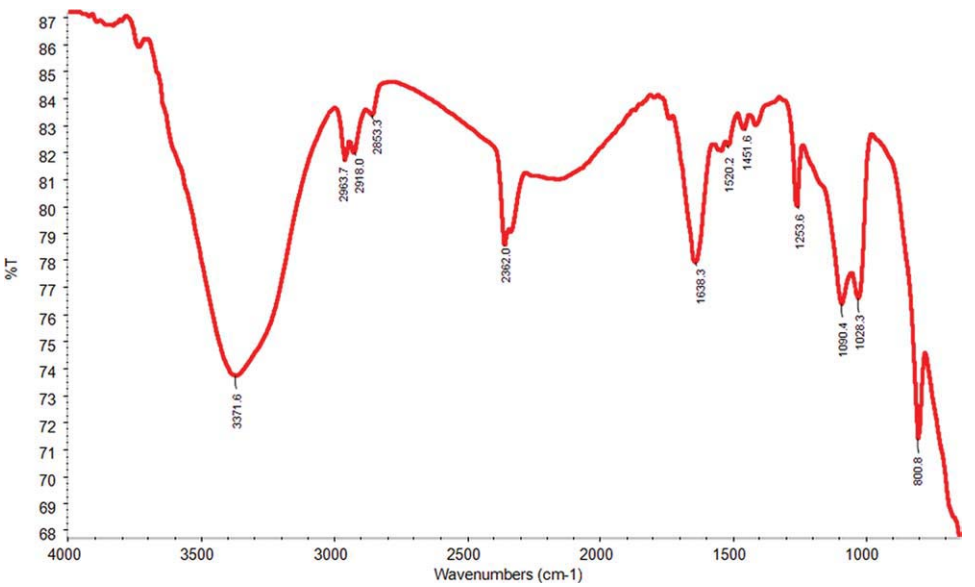

Figure 2 The infrared spectrogram of protein agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

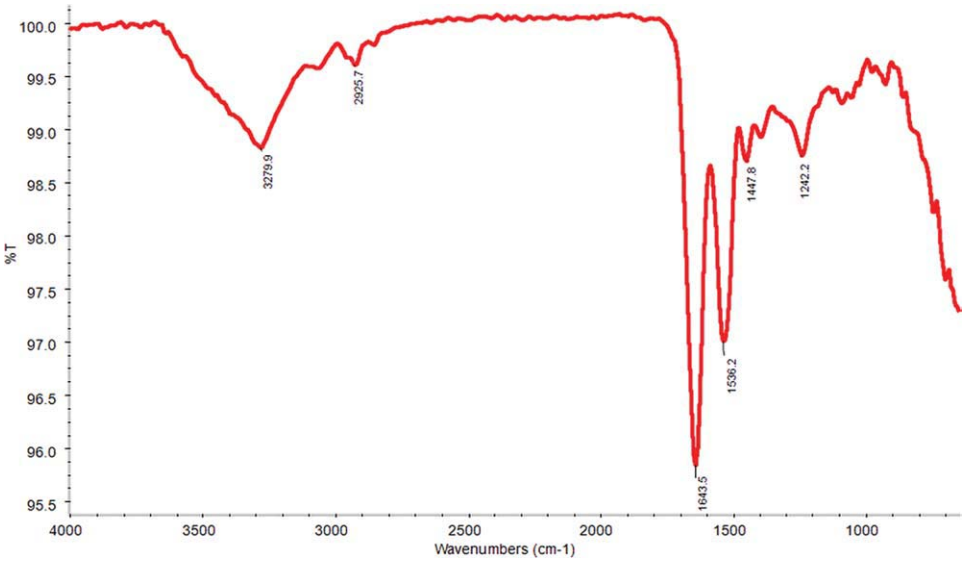

Figure 3 The infrared spectrogram of untreated wool. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intense absorption band at 3371.6 cm^{-1}, which was primarily due to the N—H stretching vibrations. The absorbing peak at 1638.3 cm^{-1} nearby, primarily governed by the stretching vibration of the C=O (70–85%) and C—N groups (10–20%), was the characteristic absorbing peak of amide I. The absorbing peak at 1520.2 cm^{-1} nearby was the characteristic absorbing peak of amide II, which was mainly derived from the in-plane N—H bending. The peak at 1253.6 cm^{-1} was associated with the amide III band. The absorbing peak at 2362.0 cm^{-1} nearby was the characteristic absorbing peak of S—H (sulfhydryl group). This confirmed the presence of protein from the IR spectrum of the chicken-feather keratin agent prepared in this study.

Change in the chemical composition of the wool treated by the chicken-feather keratin agent, plasma, and their combination

Figures 3–6 are the IR spectra of the untreated wool and the wool treated by the chicken-feather keratin agent, plasma, and their combination, respectively. When Figure 4 and Figure 3 are compared, one can see that a new absorbing peak appeared at 2358.1 cm^{-1} nearby, which was the characteristic absorbing peak of S—H (sulfhydryl group). Also, at 1095.0 and 1718.3 cm^{-1} nearby appeared new absorbing peaks. These peaks presented the C—O and C=O stretching vibrations of carboxylic groups. This indicated that carboxylic groups on the wool treated by chicken-feather keratin agent increased. Figure 4 also

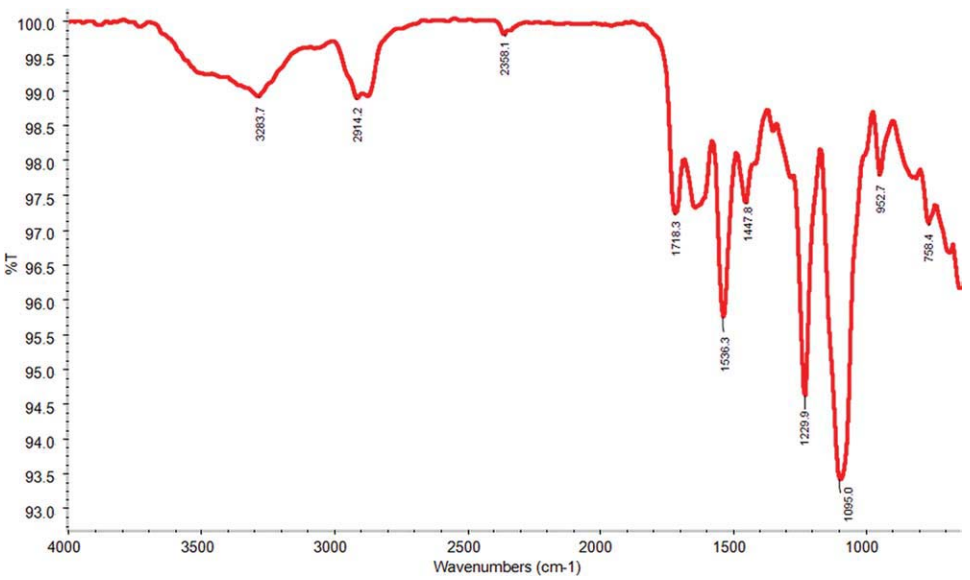

Figure 4 The infrared spectrogram of wool treated by protein agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

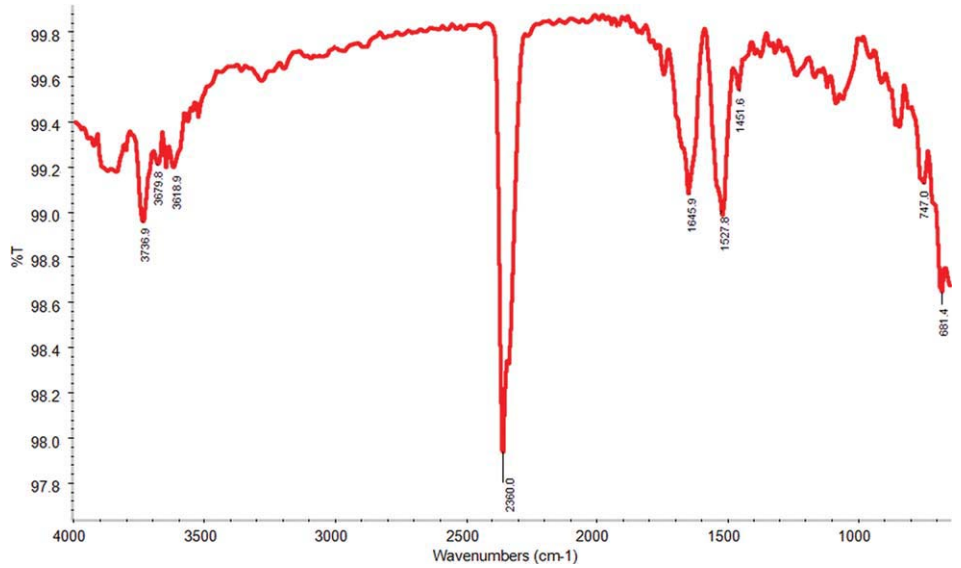

Figure 5 The infrared spectrogram of wool treated by plasma. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shows that the wool treated by chicken-feather keratin agent was similar to that of untreated wool, as both had characteristic peaks at 2920 and 1230 cm^{-1} nearby, but the absorbing frequencies decreased. This indicated that chicken-feather keratin agent connected to the wool. As shown in Figure 5, a new strong absorbing peak appeared at 2360.0 cm^{-1} nearby, in contrast to the untreated wool; this was the characteristic absorbing peak of S—H (sulfhydryl group). This shows that the surface scale of wool was partially removed by the plasma etching treatment. Three absorbing peaks appeared at the 3700 cm^{-1} nearby, which indicated that more hydroxyls and amino groups were brought on the wool treated by plasma, which led to improved wettability and dyeability of wool. When Figure 6 is compared with Figures 3, 4, and 5, one can see that more sulfhydryl groups appeared on the combined treated wool because the absorbing peak at 2358.1 cm^{-1} nearby increased. The absorptions at 1229.6 and 1092.6 cm^{-1}, corresponding to the C—N and the C—O stretching vibrations, respectively, and the absorption at 1450 cm^{-1} nearby disappeared. This showed that the content of —SH, —OH and the other polarity groups increased on the wool modified by the combination of plasma and chicken-feather keratin

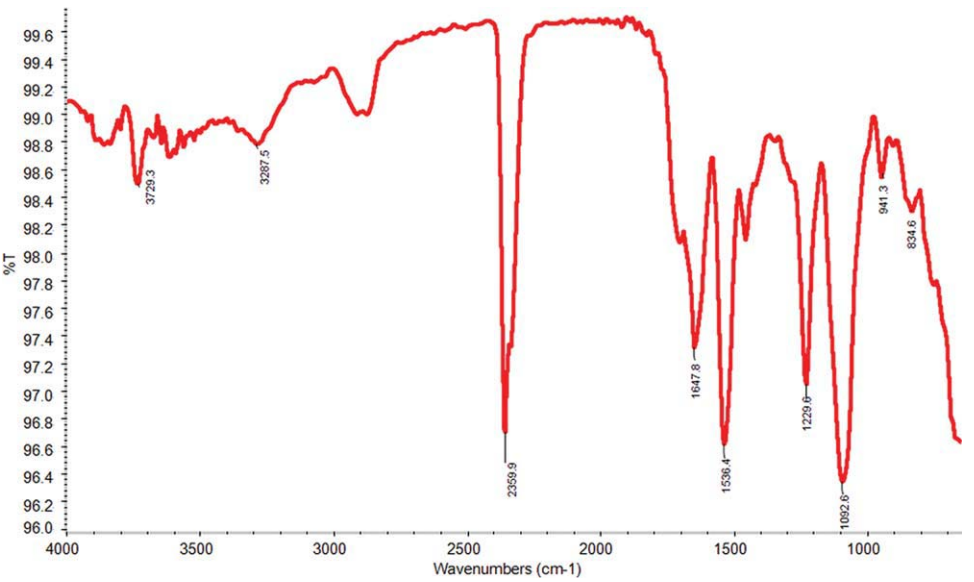

Figure 6 The infrared spectrogram of wool treated by plasma combined with protein agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

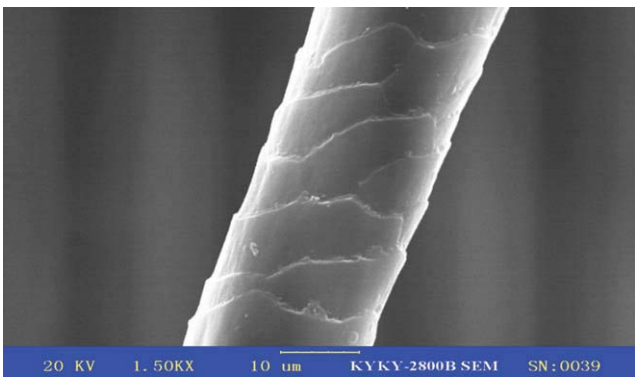

Figure 7 SEM of untreated wool. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

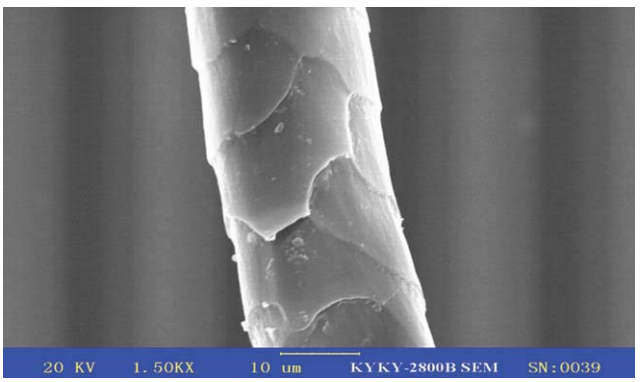

Figure 9 SEM of plasma-treated wool. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

agent; this indicated that the active wool treated by plasma was of benefit for the absorption of the chicken-feather keratin agent on it. More polarity groups were introduced into the wool, which led to an increase in the hydrophilicity of the wool.

On the basis of this analysis, we observed that wool treated by different techniques had different IR spectra; this indicated that the chemical compositions of the wools treated by the chicken-feather keratin agent, plasma, and their combination were different. We concluded that the chicken-feather keratin agent successfully fixed on the wool pretreated by plasma.

The morphological structures of the wool surfaces treated with different techniques were observed by SEM, as shown in Figures 7–9. The surface scale of the untreated wool is shown clearly in Figure 7, whereas Figure 8 demonstrates that the chicken-feather keratin agent was adsorbed on the wool, but the chicken-feather keratin agents adsorbed loosely and were not well-dispersed in the fiber, and the surface scale on the wool is not clear. Figure 9, in contrast to Figure 7, proves that the surface of the wool was partially etched by the plasma. As shown in Figure 10, more chicken-feather keratin agent was introduced into the combined treated wool than the fiber modified by chicken-feather keratin agent alone. It turned out that the chicken-feather keratin agents adsorbed closely and were better dispersed on the surface of the fiber, and the morphological structures of the fiber surface were changed, the surface scale of the wool was not clear. This indicated that plasma pretreatment facilitated the filling up of fiber cracks with chicken-feather keratin agent, which in turn, allowed a more uniform film formation on the surface. The uniform film decreased the directional fractional effect of wool, brought more dye in contact with the modified fiber, and induced the generation of more surface area for providing more spacing to the dye diffusion that occurred. This, hence, led to the improvement of the antifelting properties and dyeing behavior.

Effect of the different treatment techniques on the antifelting properties of the wool

As shown in Table I, the felt-ball density of untreated wool was the largest; its antifelting properties were the worst. The felt-ball density of the wool treated by the chicken-feather keratin agent

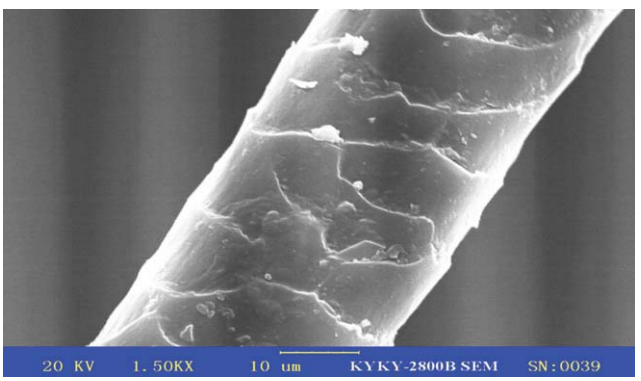

Figure 8 SEM of protein-treated wool. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

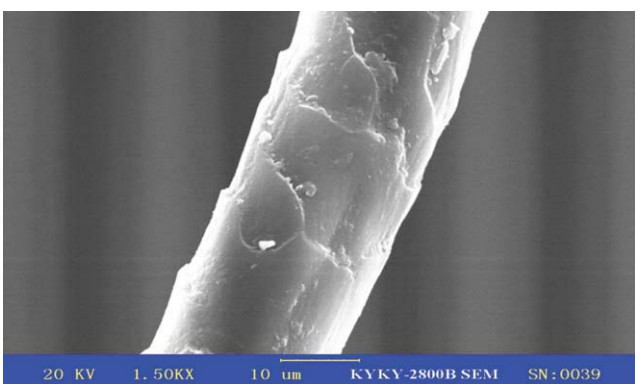

Figure 10 SEM of plasma and protein combination-treated wool. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
The Felt Ball Density of Wool Treated by Different Techniques

Sample	1	2	3	4
Felt-ball density (g/cm^3) $\times 10^{-2}$	17.9	9.9	5.3	2.4

1 = untreated fiber; 2 = treated by chicken feather keratin agent; 3 = treated by plasma; 4 = treated by the combination of plasma and chicken feather keratin agent.

TABLE III
The Dye Uptake of Wool Treated by Different Techniques (unit: %)

Dye	1	2	3	4
Lanasol Red 6G	70.33	79.90	91.22	90.92
Lanaset Blue 3G	80.46	85.16	84.06	86.98
Lanaset Red G	80.20	85.54	88.03	90.32

The meanings of the symbol of 1, 2, 3, and 4 are equal to Table I.

decreased, and its antifelting properties improved, yet the effectiveness was not obvious. The felt-ball density of the wool treated by plasma was smaller than that of the wool treated by the chicken-feather keratin agent alone; its antifelting properties were better. The felt-ball density of the wool treated by the combination of plasma and the chicken-feather keratin agent was the smallest; its antifelting properties were the best. The reason was that the lipoid substance on the surface scale was wiped off by the sputter-etching of the plasma, a part of the surface scale was damaged, and polar groups were introduced by the oxidation action of the plasma. The wetting properties and roughness of the fiber surface were all improved greatly by plasma treatment, so the antifelting properties were improved. After plasma treatment, the spreading out of the chicken-feather keratin agent on the fiber surface was favorable, and more chicken-feather keratin agent and more polarity groups were introduced on the fiber surface treated by their combination, so the wetting properties of the combined treated wool were enhanced further, and the directional frictional effect of the combination-treated wool decreased further. This led to highly improved antifelting properties. We concluded that the combination treatment by plasma and the chicken-feather keratin agent showed a good cooperating effect for improving the antifelting properties of wool. However, the treatment conditions had to be proper, for the reason that the discharged parameters of plasma would affect the chemical constituent and physical morphological structures of the wool surface and the absorption quantity of chicken-feather keratin agent on it. When the technology conditions of the plasma treatment were too strong (e.g., the discharge time was too long), the sputter-etching action of the plasma was enhanced. The polar groups introduced by the oxidation action of plasma were wiped off, which led to a reduction in the adsorption quantity of the chicken-feather keratin agent. In addition, the whiteness, strength, and wettability of the wool decreased, which resulted in the wool's quality becoming poor. Therefore, it was necessary to choose suitable modifying conditions to enhance the adsorption quantity of the chicken-feather keratin agent on the wool surface to maintain better performance in the wool.

Effects of the different treatment techniques on the wettability of the wool

The wetting power of the wool treated by different techniques is summarized in Table II The wettabilities of the untreated wool and the wool treated by chicken-feather keratin agent alone were bad, as shown in Table II. The wettability of the wool treated by plasma was the best. The wettability of the wool treated by a combination of plasma and the chicken-feather keratin agent was close to that of the wool treated by plasma (the wetting time was only 2 s) and increased greatly compared to that of the wool treated by the chicken-feather keratin agent alone. This indicates that the associated treatment of plasma and chicken-feather keratin agent overcame the shortage of bad wetting ability of the wool treated by the chicken-feather keratin agent alone.

TABLE II
The Wettability of Wool Treated by Different Techniques

Sample	1	2	3	4
Wetting time (s)	>200	>200	<1	2

The meanings of the symbol of 1, 2, 3, and 4 are equal to Table I.

TABLE IV
The Dye Depth (K/S) of Wool Treated by Different Techniques

Dye	1	2	3	4
Lanasol Red 6G	4.827	5.736	5.992	6.323
Lanaset Blue 3G	26.762	27.964	28.206	29.085
Lanaset Red G	13.832	14.178	14.286	15.874

The meanings of the symbol of 1, 2, 3, and 4 are equal to Table I.

Effects of the different treatment techniques on the dyeing ability of the wool

The dye uptake of wool treated by the different techniques and dyed with different dyes are summarized in Table III, where it is shown that the dye uptake of the wool pretreated with chicken-feather keratin agent alone or with plasma alone was higher than that of the untreated wool. The dye uptake of the wool treated by a combination of plasma and the chicken-feather keratin agent was the biggest; this indicated that combined treatment would be helpful for improving the dyeing ability of wool. The reasons were that more polarity groups, such as $-NH_2$ and $-SH$, were introduced into the treated wool, and the surface scale of the treated fiber was partially damaged, so the affinity between the dyes and the fiber treated by a combination of plasma and the chicken-feather keratin agent increased, and the rate of dye diffusion into the fiber increased, too. This led to the adsorption of more dye, so the dyeing ability of the fiber treated by plasma combined with the chicken-feather keratin agent improved dramatically and could have decreased the dyeing temperature.

Table IV demonstrates that the dye depth of the wool pretreated with chicken-feather keratin agent alone or with plasma alone was enhanced compared with that of the untreated wool, but the dye depth of the wool treated by the combination was the biggest among the dye depths of the wools treated by the three techniques and dyed with the three experimental dyes. This indicated that the combination treatment saved the quantity of dyes.

CONCLUSIONS

Chemical constituent and physical morphological surface structures were different when the wools were treated by chicken-feather keratin agent, plasma, and their combination, respectively. This showed that the content of $-SH$, $-OH$, and other polarity groups increased in the wool modified by the combination of plasma and chicken-feather keratin agent. It also indicated that the active wool treated by plasma was of benefit for the absorption of chicken-feather keratin agent. The surface scale of the treated wool was not clear; this led to a decrease in the directional frictional effect of the wool. With the different treatment techniques, the wool exhibited various behaviors because of the changes in the chemical and physical structures. The antifelting performance, wetting properties, and dyeing behavior of the treated wool top were better than those of the untreated wool top. The wool top treated by the combination of plasma and chicken-feather keratin agent had the best antifelting performance, wetting power, and dyeing ability. The associated treatment technique of plasma and chicken-feather keratin agent was advantageous, as it could not only improve the performance of wool but also turn waste to treasure and reduce environmental pollution.

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