Chen, Weiguo, Chen, Dongzi and Wang, Xungai 2001-05, Surface modification and bleaching of pigmented wool, *Textile Research Journal*, vol. 71, no. 5, pp. 441-445.

Surface Modification and Bleaching of Pigmented Wool

Weiguo Chen, Dongzi Chen, Xungai Wang[#]

School of Materials and Textiles, Zhejiang Institute of Science and Technology

Hangzhou 310033, P. R. China

[#]School of Engineering and Technology, Deakin University

Geelong 3217, Australia

ABSTRACT

We treated naturally pigmented karakul wool with surface modification of chlorination and catalytic bleaching. We examined the structure and properties of the treated wool. We took SEM photos to reveal the surface morphology of karakul wool and used Allwörden reaction to show the extent of damage to the epicuticle of the wool. The results showed that the surface modification removed the bulk of the fiber scales and bleaching led to an increase in fiber whiteness. After bleaching, the felting propensity of karakul wool improved slightly and its dye uptake reduced. For modified-cum-bleached karakul wool, its felting propensity reduced, dyeing rate increased and equilibrium exhaustion decreased, compared with untreated karakul wool.

Chlorination, plasma treatment and other oxidising methods without AOX are currently available to modify wool to improve its surface smoothness and reduce the fiber diameter, so that we can obtain soft, lustrous and even machine washable wool products [10, 11, 14]. For bleaching of pigmented animal fibers, there has been considerable development in the last 20 years [1, 2, 3, 5, 13, 15]. In this study, we treated dark brown karakul wool with DCCA in saturated salt solution to remove fiber scales wholly or partially at first, then bleached the fiber with catalytic bleaching. We reported the effect of these treatments on some structure and properties of the karakul wool.

Experimental

MATERIALS

We used scoured dark brown karakul wool (loose stock) in the experiment. We cleaned the wool by Soxhlet extraction with ethyl ether for 5 hours before all experiments. All chemicals are AR grade. Chloridizing reagent Basolan DC (DCCA) was from BASF.

METHODS

Modification with chlorination

We treated the karakul wool with an acid solution (NaCl 310g/L, HCl 20ml/L, wetting agent 0.5 g/L) at 20^{o}C for 5 minutes, then treated it with chlorination (NaCl 310g/L, DCCA 8%owf, wetting agent 0.5g/L) at 22^{o}C for 20 minutes, finally we did dechlorination with $NaHSO_3$ (3 g/L) for 30 minutes and rinsed the sample for 40 minutes. The liquid-to-wool ratio was 20:1.

Bleaching process

We treated the wool with following process:

Mordanting with Fe^{2+} $\rightarrow$ Rinsing $\rightarrow$ Bleaching with H_2O_2.

Mordanting: The mordanting bath consisted of $FeSO_4 \bullet 7H_2O$ (10g/l), HCOOH (6g/l), and wetting agent (0.5g/l). We raised the bath to 80^{o}C and kept it at 80^{o}C for 60 minutes.

Rinsing: We used HCOOH (4g/l) solution to rinse the mordanted samples at 80^{o}C for 20 minutes and then rinsed it with water from 80^{o}C to 50^{o}C within 20 minutes, followed by a final rinsing with water from 50^{o}C to room temperature in 30 minutes.

Bleaching: Following the rinsing, we bleached the wool in the solution of H_2O_2 (30%w/w, 50~60g/l), Tetrasodium pyrophosphate (10 g/l), Oxalic acid (4g/l), Sodium Carbonate (5g/l), and wetting agent (0.5g/l). We maintained the pH at 8.0~8.5 with ammonia solution. We carried out the treatment at 68~70^{o}C for 45 ~60 minutes. The liquid-to-wool ratio was 20:1.

Measurement of whiteness

We combed the loose stock sample and pressed it in a disk and measured the whiteness with ZBD Whiteness Meter.

Measurement of tensile properties

We used a single fiber analysis meter to measure the strength and elongation at break, and tested a total number of 300 fibers for each sample.

Weight loss

Before and after the bleaching, we accurately weighed the samples. With another parallel sample, we measured the moisture regain of the samples before and after the treatments. From that, we obtained the absolute dry weight of the samples, and calculated the weight loss.

SEM analysis

We used Type JEOJL JSM-35C Scanning Electron Microscope to observe and photograph the structure of fiber scales.

Allwörden reaction

We exposed the fibers to freshly prepared saturated bromine water while observing the fibers with a microscope. We then took the photos with a digital camera.

Measurement of dye exhaustion

We used purified C. I. Acid Red 1 in this experiment. We prepared two dye-bathes with the same concentration (1.5%owf), same pH2.08 (adjusted with H_2SO_4) and same liquid-to-wool ratio (100:1) in two 3-neck flasks which were fitted with water cooling worm. We then heated flasks to 85^{o}C in water bath. We put two samples into the dye-bathes and stirred the samples occasionally. At 0, 5, 10, 20, 30, 60, 90 minutes during dyeing, 2ml dyeing solution was drawn from one dye-bath and the same amount of dyeing solution from another one was transferred into the flask to keep the liquid ratio. We diluted the drawn solution to 25ml and measured its absorbance in type 721 spectrophotometer at the maximum absorption length λ_{max} of each dye. The dye exhaustion was expressed as the percent decrease of concentration in the dye bath (Equation 1):

$$E = (1 - A_i / A_0) \times 100 \qquad (1)$$

Where E is the dye exhaustion (%), A_0 and A_i are the optical density of the initial dyeing solution and the dyeing solution at different dyeing time, respectively.

Test of felting property

We used SDM2-140 Sample Dyeing Machine (Fong's) for the tests. We put 1.0g of wool sample into the stainless steel dyeing cylinder in which 50ml of 1% Lamepon A solution and 5 small steel balls were added. The dyeing cylinder was rotated at 45^{o}C for 75 minutes to form the felt ball. We rinsed the sample gently with cold water and dried it at 60^{o}C, and then conditioned it at atmosphere for 12 hours. We measured the diameters of felt balls in 12 directions with a micrometer and calculated the average.

RESULTS AND DISCUSSION

WHITENESS, TENSILE PROPERTIES AND LOSS OF WEIGHT

In Table 1, we list the results of whiteness, single fiber strength and elongation at break, the loss of weight before and after the bleaching.

Table 1 Effect of bleaching on fiber whiteness, tensile properties and weight loss

Fibres	Whiteness (%)		Strength (CN)		Elongation(%)		Loss of Weight (%)
	Before	After	Before	After	Before	After	
Karakul Wool	9.20	40.46	6.56	5.54	39.97	36.80	5.16
Modified Karakul Wool	7.80	37.05	6.29	5.16	38.66	37.56	10.17
White Cashmere	48.88		4.06		45.10		/

Table 1 shows chloridizing modification made karakul wool a little darker. In order to compare the whiteness, we also measured the original white cashmere under the same condition and its whiteness reading was 48.88%. We bleached the karakul wool to 40.46% in the low-cost process chosen for this study, in which we only used formic acid to keep most iron in ferrous form without using any reducing agent. The treated karakul wool was white enough to be dyed to pastel hue. The modification of wool in saturated salt solution was almost limited to the surface scales [14]. Consequently, the loss of single fiber strength was small (4.12%). For unmodified karakul wool, the single fiber strength dropped by about 15.54% after bleaching. The dissolution of pigment itself did not cause degradation of the long chain of wool keratin. The Fe^{2+}--pigment interaction is much stronger than the Fe^{2+}--keratin interaction [3, 8]. If absorbed iron is completely removed from the fiber keratin, the attack of radicals will be localised exclusively at the pigment, while the wool keratin undergoes only a simple peroxide bleaching [3]. The degradation of keratin is still unavoidable even if it is a simple peroxide bleaching. However, bleaching destroyed the pigments in the fiber, leaving tiny cavities throughout the fiber [3]. The degradation of keratin and the creation of the cavities are the main causes of fiber strength loss after bleaching. The loss of single fiber strength due to bleaching wool was much greater than that caused by controlled surface modification only. For modified karakul, the reduction in strength is 17.96 % after bleaching according to results in Table 1. This reduction is higher than that of unmodified wool. Apparently, the modified karakul wool experienced severer damage in bleaching. But the bleached-cum-modified wool still has higher strength than the white cashmere. Table 1 also gives results on changes in fiber elongation. Both bleaching and modification reduced fiber elongation, but the reduction in elongation due to bleaching was less for modified karakul wool than the unmodified wool. We may infer from the results that the removal of the hard and dense scales contributed to the smaller reduction in elongation for the modified karakul wool. Because of the second chemical treatment, the modified-cum-bleached karakul lost more weight from its interior and surface (Table 1).

SEM ANALYSIS

A considerable amount of literature exists in the area of modification and bleaching of wool. McPhee and Rushforth [12,14] state that the surface modification of wool in saturated salt solution is the most effective because the swelling of wool was inhibited. Figure 1 shows the SEM photos of the surface morphology of wool and cashmere. The modification removed the bulk of scales. Figure 1(c) shows modified wool has a much smoother surface than the untreated one shown in Figure 1(a). A smooth surface will increase the specular reflection of light [14]. Figure 1(e) is the SEM photo of the white cashmere. Cashmere has a smooth surface, so it appears lustrous. Figure 1(b) shows that catalytic bleaching did not modify the surface of wool and the scale structure remained almost intact without noticeable damage. Some water-soluble material would have been dissolved in the strong oxidation process and the scale edges may become sharper. After modification, the surface structure of wool became weak because of the removal of scales. In the second chemical treatment, hydrogen peroxide (H_2O_2) brushed the remaining scales, resulting in a smooth fibre surface as shown in Figure 1(d).

ALLWÖRDEN REACTION

In Allwörden reaction, epicuticle forms sacs only on the outer surface of cuticle cells and not at all on cortical cells [9]. So we can use Allwörden reaction to test the damage extent of epicuticle. In Figure 2(a), almost regular and continuous sacs formed on the untreated karakul, although it may not be so regular on other individual fibers because of the damage caused by weathering and processing [7]. Figure 2(b) shows the sacs formation on the bleached karakul, indicating that much of the epicuticle remained after the bleaching. Figure 2(c) and 2(d) showed no Allwörded reaction on modified karakul and modified-cum-bleached karakul wool, clearly suggesting that most scales were removed in these cases.

FELTING PROPENSITY

Table 2 gives the results of test of felting propensity. The diameter of felt ball of bleached karakul wool is slightly smaller than that of unbleached karakul. As mentioned above, bleaching may increase the sharpness of scale edges. So the felt propensity of bleached karakul may increase slightly. For modified karakul, the bulk of scales were removed, and it was unable to form felt ball in the test. The same result happened for modified-cum- bleached karakul wool.

Table 2. Diameter of Felt Ball

Diameter(cm)	Karakul	Modified Karakul
Unbleached	2.111	No ball formed
Bleached	1.998	No ball formed

DYEING AND PROPERTY

Figure 3 shows the dyeing property of untreated karakul, modified karakul, bleached karakul and modified-cum-bleached karakul with C. I. Acid Red 1. We can see that the modified karakul wool absorbed dye more quickly than untreated karakul wool, and its equilibrium exhaustion increased slightly after modification. It is easy to understand the increase of dyeing rate and equilibrium exhaustion because of the removal of scales, which reduced the resistance to the penetration of dye into wool and ruptured the protein chain which produced more $–NH_3^+$ in acid condition. But bleaching decreased the dye uptake. In bleaching, the disulphide bond was oxidised by H_2O_2, with one cystine residue forming two cysteic acid residues [4]. The cysteic acid residue RSO_3^- repelled the negative ions of acid dye and so caused the reduced dye uptake. For modified-cum-bleached karakul wool, its dyeing rate increased but equilibrium exhaustion decreased. The removal of scales reduced the resistance layer to the penetration of dye and so the dyeing rate increased. But the damage of keratin by bleaching produced more cysteic acid residue RSO_3^-, so that the equilibrium exhaustion decreased further.

CONCLUSION

With the modification and bleaching, we may use the relatively cheap naturally pigmented karakul wool to produce lustrous, soft and colourful fabrics. The surface modification used in this work removed the bulk of scales and resulted in only a small degree of damage in fiber tensile properties. The bleaching led to an increase in fiber whiteness and did not cause apparent change in the surface morphology of karakul wool. Even though the fiber epicuticle remained almost intact after bleaching, further loss in fiber strength occurred. Nevertheless, the modified-cum-bleached karakul wool still had greater strength than the white cashmere. After bleaching, the felting propensity of karakul wool improved slightly, and its dye uptake reduced. The modified-cum-bleached karakul wool has a smooth surface, which reduces its felting propensity. It also has increased dyeing rate and reduced equilibrium exhaustion. After such treatment, we may use this relatively cheap wool to produce lustrous and shrinkage-resistant worsted goods with soft handle and pastel shade. For full shrinkage resistance, additional polymer application will still be necessary.

ACKNOWLEDGMENT

We wish to acknowledge the Committee of Science and Technology of Zhejiang Province and Committee of Science and Technology of Hangzhou City and Hangzhou No.2 Woollen General Mill (P. R. China) for the financial support. We also wish to acknowledge Pao Yu-kong and Pao Zhao-long Scholarship for Chinese Students Studying Abroad for sponsoring the first author's visit to Australia.

Literature Cited

1. Arifoglu, M. and Marmer, W. N., Sequential Oxidative and Reductive Bleaching of Stained and Pigmented Wool in a Single Bath, *Textile Res. J.* **60**, 549-554 (1990).
2. Bereck, A., Bleaching of Dark Fibres in Wool, in "Proc. 7th Int. Wool Text. Res. Conf.,Tokyo," vol. IV, 1985, pp. 152- 161.
3. Bereck, A., Bleaching of Pigmented Speciality Animal Fibres and Wool, *Rev. Prog. Color*. **24**, 17-25 (1994).
4. Cegarra, J. and Gacen, J., The Bleaching of Wool with Hydrogen Peroxide, *Wool Science Review*, **59**, (1983).
5. Earland, C. and Little, A. S., The Bleaching of Naturally Pigmented Cashmere with Hydrogen Peroxide, in "Proc. 7th Int. Wool Text. Res. Conf., Tokyo," vol. IV, 1985, pp. 130-140.

6. Fraser, R. D. B. and Rogers, G. E., The Bromine Allworden Reaction, *Biochim. Biophys.Acta* **16**, 307-316 (1955).

7. Gregorski, K. S. and Pavlath, A. E., Fabric Modification Using the Plasmod, *Textile Res. J.* **50**, 42-46 (1980).

8. Laxer, G. and Whewell, C. S, Some Physical and Chemical Properties of Pigmented Animal Fibers, in "Proc. Int. Wool. Res. Cong. Australia," vol. F, 1955, pp. 186-200.

9. Leeder, J. D., The cell membrane complex and its influence on the properties of the wool fibre, *Wool Science Review* **63** (1987).

10. Makinson, K. R., "Shrinkproofing of Wool", Marcel Dekker Inc., New York, 1979.

11. Mcphee, J. R., & Shaw, T., The Chemical Technology of Wool Processing, *Rev. Prog. Color*. **14**, 58-68 (1984).

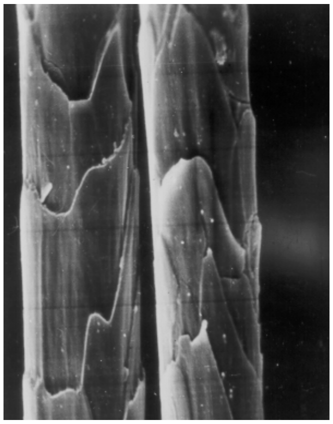
12. McPhee, J. R., Shrinkproofing of Wool with Neutral Permanganate or Acid Bromate in Concentrated Sodium Chloride Solution, *Text. Res. J*. **30**, 358-365 (1960).

13. Oh, K., Park, M. and Kang, T., Effect of mordant bleaching on the optical and mechanical properties of black human hair, *J. Soc. Dyers Colour*. **113**, 243-249 (1997).

14. Rushforth, M., Soft Handle Treatments for Wool, *Wool Science Review* **67** (1991).

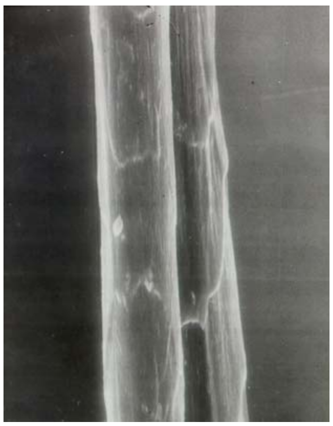
15. Trollip, N. G., Maasdorp, A. P. B. etc., A Study of the Mordant Bleaching of Karakul, in " Proc. 7th Int. Wool Text. Res. Conf., Tokyo," vol. IV, 1985, pp. 141-151.

List of figures:

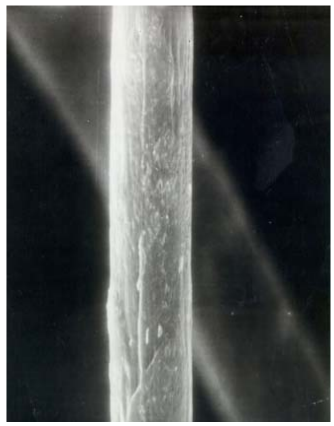


(a) Untreated karakul

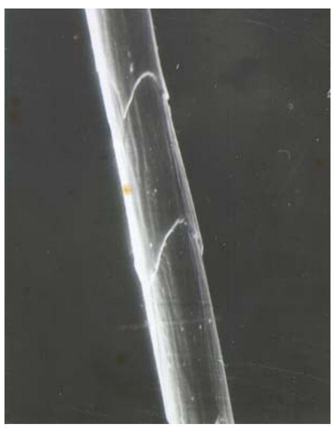
(b) Bleached karakul



(c) Modified karakul



(d) Modified-cum-bleached karakul



(e) White cashmere

Figure 1: SEM photos of different fibers

(a) Untreated karakul

(b) Bleached karakul

(c) Modified karakul

(d) Modified-cum-bleached karakul

Figure 2: Photos of Allwörden reaction

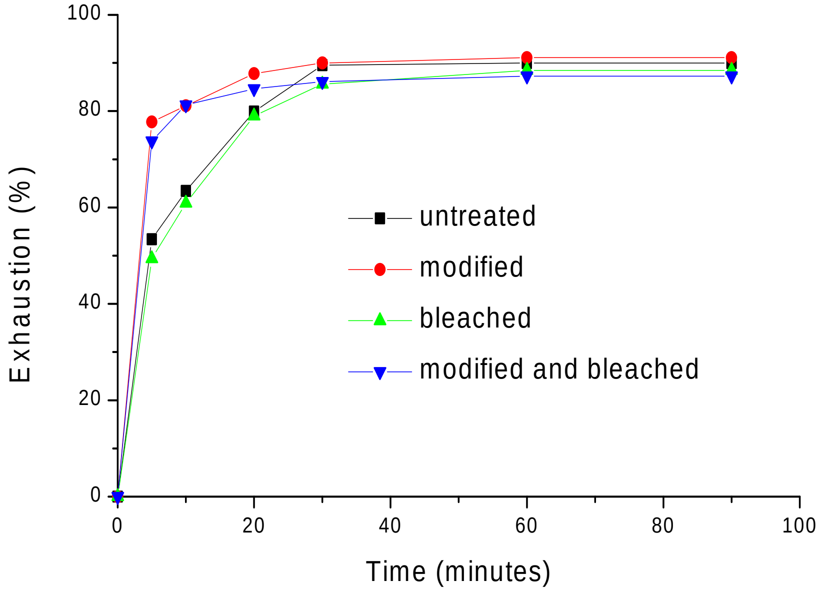


Figure 3. Dyeing property of karakul wool with C. I. Acid Red 1