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Comparison of the Structure and Properties of Wool and Cashmere Fibers under Potassium Permanganate Treatment

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Abstract
In this study, the weight loss and tensile property of wool fibers and cashmere fibers before and after various potassium permanganate solution treatment were investigated. The scale morphology and crystallization index of the original and treated fibers were analysed with scanning electron microscopy and X-ray diffraction analysis. The experimental results showed that the weight loss of wool fibers is more than that of cashmere fibers under low potassium permanganate content treatment, but is less than that of cashmere fibers under high potassium permanganate content treatment. The force loss of cashmere fibers increased linearly with an increase in potassium permanganate content. The scales of cashmere fiber were damaged at a potassium permanganate content of 9%, but the scales of wool fiber were clear. The relative crystallisation index of treated wool is twice as that of treated cashmere at a potassium permanganate content of 9%.

Key words: *wool fibers, cashmere fibers, potassium permanganate, scale, force loss.*

Introduction

Both wool and cashmere fibers are a natural protein fiber that has been widely used as a high-quality textile material. The two fibers consist of a scale layer and cortical layer. It is reported that cashmere fiber has a thin scale layer and low scale density compared with wool fibers [1]. The scales play a very important in protecting the properties of animal fibers. It consists of lamellar keratinocytes, including a surface lipid layer, epicuticle layer and endocuticle layer. Epicuticle has a lot of cysteine, including a disulfide bond [2]. However, the scales of wool and cashmere fibers are believed to make a major contribution to the felting shrinkage of products made from them. The felting or entanglement of animal fibers is a unique property of many of them. However, the felting property influences the appearance and dimensional stability of products [3]. Studies on wool fiber anti-felting treatment have been reported widely. One of the most important developments in shrink-resistance or anti-felting treatments for wool has been the Hercosett process. This process involves a mild chlorination treatment to modify the surface properties of wool fibers, followed by the application of a cationic polyamide [4]. SEM demonstrates different minor etching effects of low temperature plasma treated cashmere fibers [5]. As an oxidising agent, potassium permanganate ($KMnO_4$) is nontoxic and usually used for sterilisation in medicine. Potassium permanganate was used for wool fiber shrink-proof treatment [6,7]. Li also reported the anti-felting treatment of cashmere fibers using the potassium permanganate oxidising method[8]. In this work, wool and cashmere fibers were treated using potassium permanganate solution under the same treatment conditions to investigate the degree of the effect of potassium permanganate treatment on the scale morphology and tensile force of wool and cashmere fibers.

Experimental

Materials

China white cashmere fibers and Australian white wool fibers were selected for the experiment.

The disulfide bond and peptide bond of the scales of wool fibers and cashmere fibers are oxidative scissions because they react with potassium permanganate solution with another auxiliary at a special temperature, producing MnO_2 deposits on the surface of the fibers, which leads to the fibers browning [9]. Fibers treated by potassium permanganate solution are reduced using a reducing solution with sodium sulfite and acetic acid so that the brown deposited on the surface of the fibers is removed through the chemical reaction.

The process of potassium permanganate ($KMnO_4$) solution treatment is as follows:

Fibers → $KMnO_4$ solution treatment → washing (three times with water at 30 °C) → sodium sulfite solution reduction (30 g/l sodium sulfite and 20 ml/l acetic acid for 15 min at 45 °C → washing (three times with water at 30 °C) → drying (in an oven at 85 °C up to content weight)

Potassium permanganate solution treatment conditions: potassium permanganate (1%, 3%, 5%, 7%, 9%, 11%, and 13%, respectively) with sodium pyrophosphate 1% at 40 °C for 40 min. Bath ratio = 1:30, pH = 3.

Test

The wool and cashmere fibers were treated in potassium permanganate solutions. Assuming the weights of fibers before and after potassium permanganate solution treatment as W_0 and W_1, the weight loss percentage(R) was calculated using ***Equation (1)***.

$$R\,(\%) = [(W_0 - W_1)/W_0] \times 100\% \qquad (1)$$

The tensile property of a single fiber before and after potassium permanganate solution treatment was tested using a YG001 single fiber tensile tester (Taicang Textile Apparatus Co., China). The test length of fiber was 10 mm and the tensile speed 10 mm/min. 100 fibers were tested for each result. Assuming the breaking force of a single fiber before and after potassium permanganate solution treatment as S_0 and S_1, and elongation at break of a single fiber before and after potassium permanganate solution treatment as ε_0 and ε_1, the strength loss and elongation at break loss of a single fiber were calculated using ***Equation (2)*** and ***Equation (3)***, respectively.

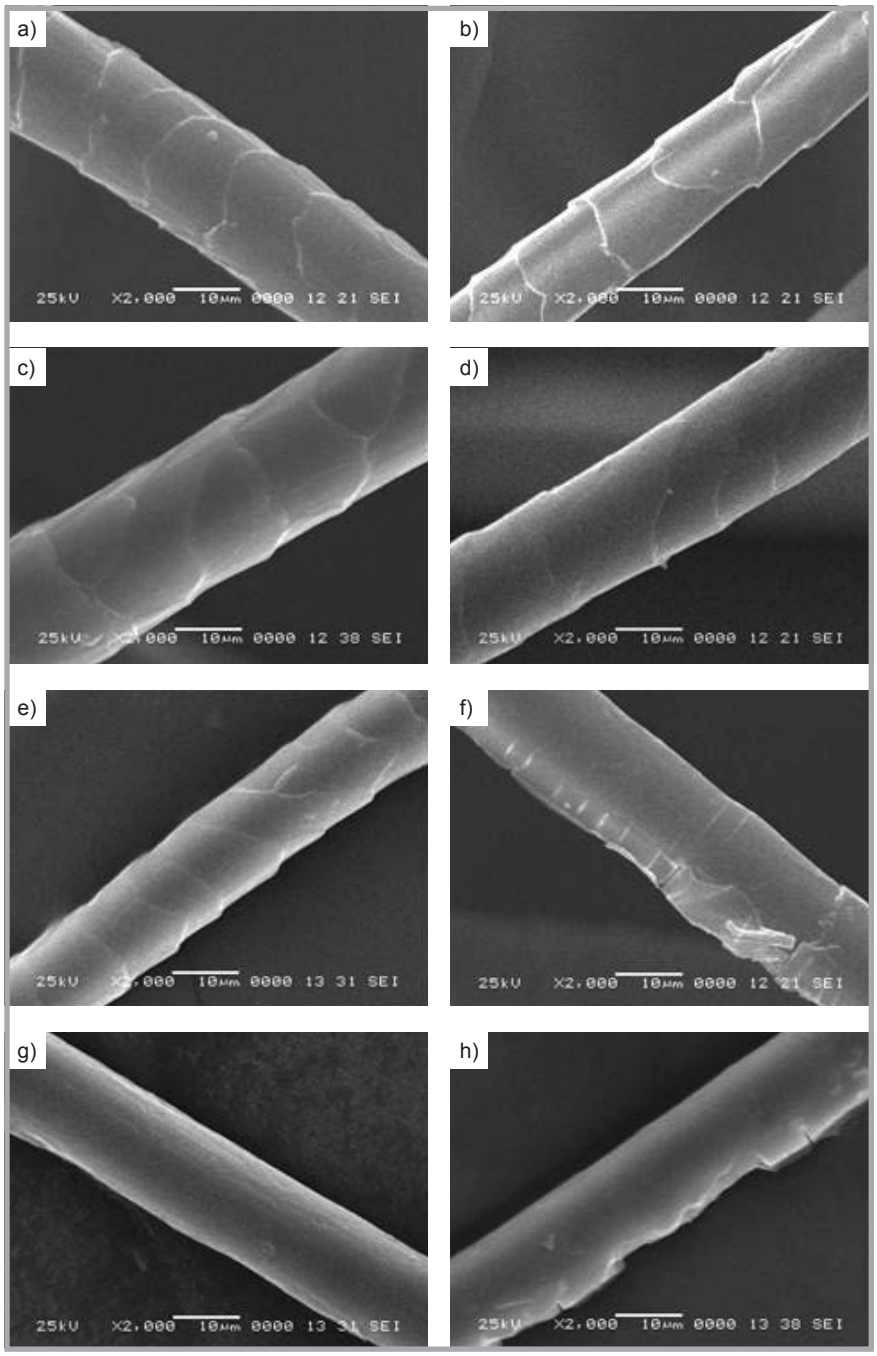

Figure 1. *Scales of fibers: a) original wool morphology, b) original cashmere morphology, c) wool treated ($KMnO_4$ content = 3%), d) cashmere treated ($KMnO_4$ content = 3%), e) wool treated ($KMnO_4$ content = 9%), f) cashmere treated ($KMnO_4$ content = 9%), g) wool treated ($KMnO_4$ content = 13%), h) cashmere treated ($KMnO_4$ content = 13%).*

Table 1. *Weight loss and tensile property of the fibers.*

Potassium permanganate content/%	Weight loss/%		Force loss/%		Elongation at break loss	
	Wool	Cashmere	Wool	Cashmere	Wool	Cashmere
1	0.75	0.65	1.78	2.1	3.25	5.21
3	1.08	0.86	1.87	3.3	5.96	7.54
5	2.38	1.62	2.1	6.06	7.57	9.43
7	3.03	2.49	3.07	10.48	11.59	11.92
9	3.94	4.11	5.45	13.09	12.62	15.08
11	4.89	5.4	6.28	16.84	13.94	17.7
13	5.74	7.07	10.18	18.5	15.21	19.35

$$\text{Force loss (\%)} = [(S_0 - S_1)/S_0] \times 100\% \quad (2)$$

$$\text{Elongation at break loss (\%)} = [(\varepsilon_0 - \varepsilon_1)/\varepsilon_0] \times 100\% \quad (3)$$

The fiber surface morphology was observed using a JSM-6460LV scanning electronic microscope (JEOL Co., Ltd., Japan). The fibers were coated with gold, and then testing was done.

The infrared spectrum was tested using a Nicolet 5700 tester (Thermo Nicolet Corporation, USA). The fiber was cut into powder, then mixed with KBr, and a round thin sheet was made as a test sample. Wave number scanning scope = 4000 cm^{-1} – 500 cm^{-1}.

The crystallinity of the fibers was tested with a D/MAX-2400 X-ray diffraction analyser (Rigaku Co. Ltd., Japan). The test conditions were as follows: voltage 546 kV, current 5100 mA, Cu Kα radiation, scanning scope 2θ = 5° – 40°, and scanning speed = 4°/min.

According to ref. [10], the crystallisation index (CI) of fibers is calculated by the following ***Equations (4), (5)***:

$$CI = (I_{9^\circ} - I_{14^\circ})/I_{9^\circ} \quad (4)$$

Where I_{9° is the intensity at 2θ = 9° and I_{14° at 2θ = 14°.

$$\text{Relative CI (\%)} = [\text{CI of the fibers treated/CI of the original fibers}] \times 100\% \quad (5)$$

The X-ray photoelectron spectroscopy (XPS) of the fibers was tested using a K-ALPHA instrument (VG, Co., United Kingdom). Test conditions: 12 KV, 6 mA.

Results and discussion

Weight loss

The weight loss of fibers under various potassium permanganate contents is shown in ***Table 1***. The weight loss of wool fibers is more than that of cashmere fibers with a low potassium permanganate content. The weight loss of cashmere fibers is more than that of wool fibers when the potassium permanganate content is 9%. Only the scales of cashmere is damaged at a low potassium permanganate content (see ***Figure 1.d***), but the fiber stem is damaged at a high potassium permanganate content (see

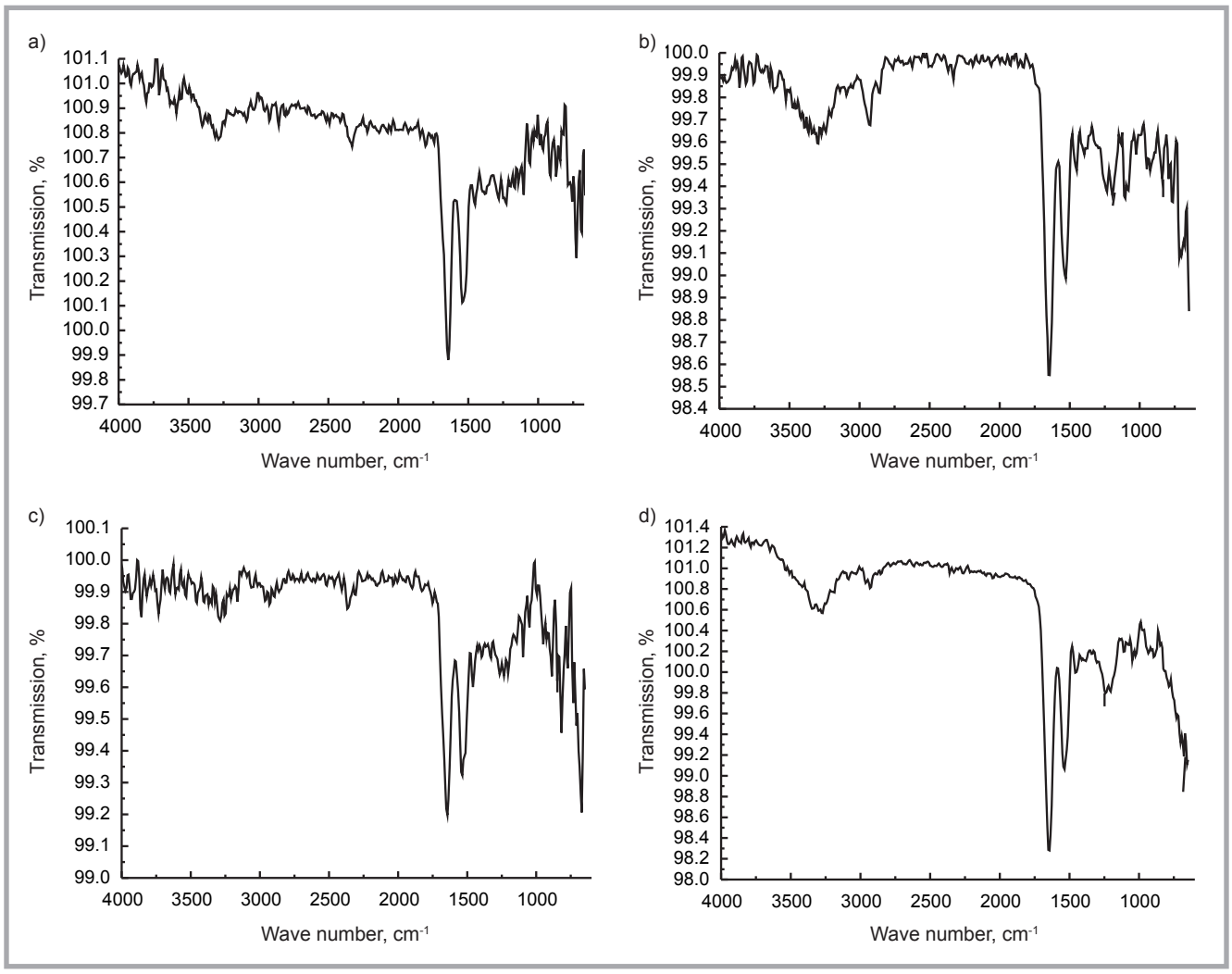

Figure 2. *Infrared spectrum graphics of the fibers: a) original wool fiber, b) wool treated ($KMnO_4$ content = 9%), c) original cashmere fiber, d) cashmere treated ($KMnO_4$ content = 9%).*

Figures 1.f, ***1.h***). Because the scale density (the scale number along the fiber length) of wool fiber is bigger than that of cashmere fiber(see ***Figures 1.a***, ***1.b***), cashmere fibers are seriously damaged at a high potassium permanganate content, and the weight loss is also increased.

Tensile property

The force loss and elongation at break loss of a single fiber with various potassium permanganate contents are also shown in Table 1. The force loss of cashmere fiber is more than that of wool fiber, which increases linearly with an increase in potassium permanganate content, due to the fiber stem being seriously damage. The elongation at break loss of cashmere fiber is slightly higher than that of wool fiber.

Fiber scale morphology

Figure 1 shows the scale morphology of the fibers. The scale density of the original wool fiber is more than that of the original cashmere fiber. The scales of wool and cashmere fiber are clear. When the potassium permanganate content is 3%, the scales of wool fiber are clear, but those of cashmere fiber are not. When the potassium permanganate content is 9%, the scales of wool fiber are visible, while cashmere fiber is damaged, and no scales are seen. When the potassium permanganate content is 13%, the scales of wool fiber are stripped off, but the fiber stem is not damaged, while the cashmere fiber stem is seriously damaged. Thus cashmere fibers are easily damaged by potassium permanganate solution, especially high potassium permanganate content solution.

Infrared spectrum

Infrared spectrum graphics of the fibers are shown in ***Figure 2***. The infrared spectrum transmission of the original wool fibers is almost the same as that of the wool fibers treated ($KMnO_4$ content = 9%), which shows that wool fibers are not seriously damaged when the $KMnO_4$ content is 9%. From ***Figure 1.e***, scales of the wool fibers treated ($KMnO_4$ content = 9%) are slightly damaged. The absorption peak (wave number = 2361 cm^{-1}) of the cashmere fibers treat-

Table 2. *CI and Relative CI values of the fibers.*

Fibers	$I_{9°}$	$I_{14°}$	CI	Relative CI/%
Original wool	232	180	22.41	100
Wool treated ($KMnO_4$ content = 9%)	241	191	20.75	92.59
Original cashmere	278	198	28.78	100
Cashmere treated ($KMnO_4$ content = 9%)	231	201	12.99	45.14

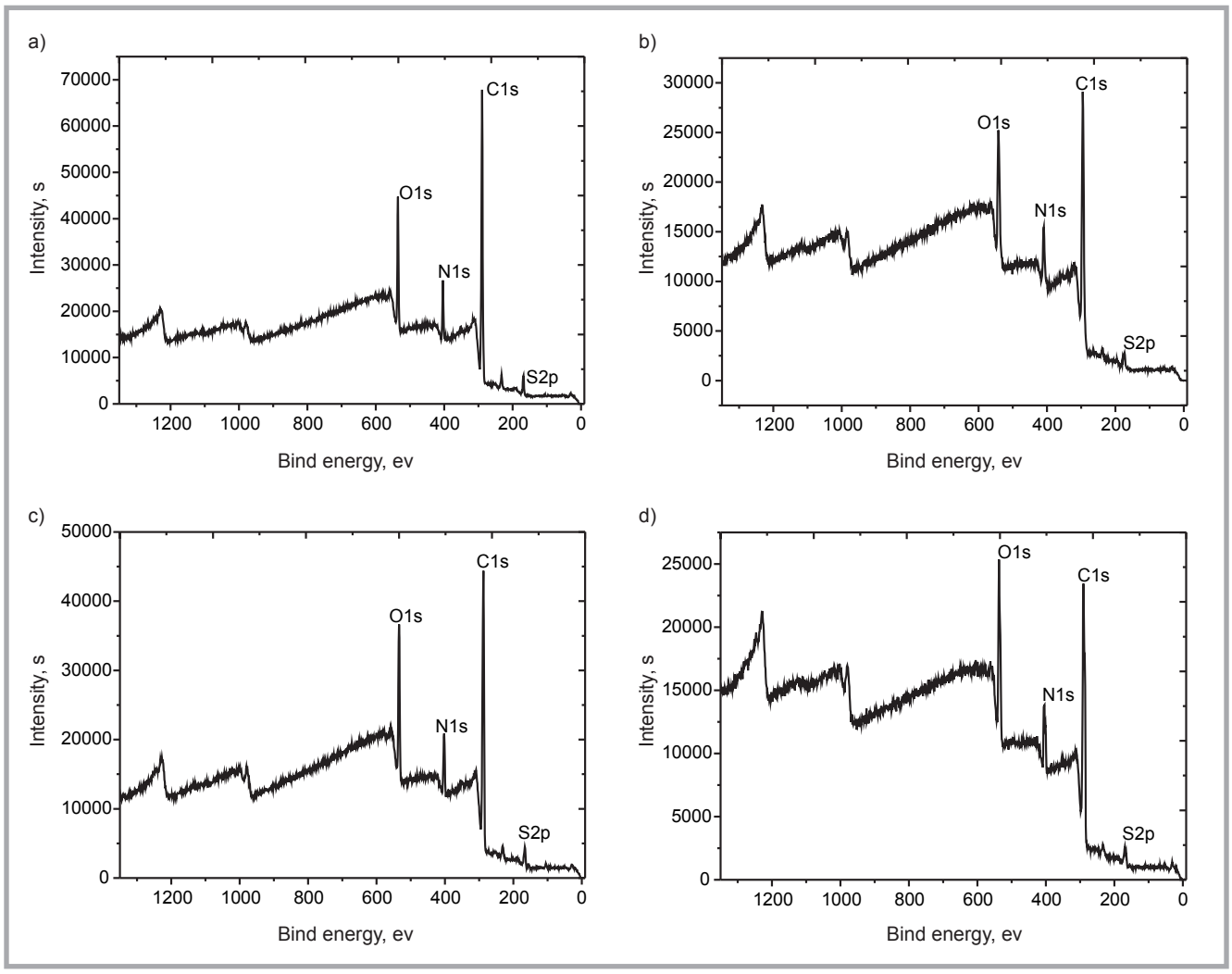

Figure 3. *XPS of the fibers: a) XPS of the original wool fibers, b) XPS of the wool fibers treated ($KMnO_4$ content = 9%), c) XPS of the original cashmere fibers, d) XPS of the cashmere fibers treated ($KMnO_4$ content = 9%).*

Table 3. *Element contents of the fibers.*

Fibers	Peak location/ev				Element			
	C1s	N1s	O1s	S2p	C1s	N1s	O1s	S2p
Original wool fibers	288.7	403.4	535	167.6	76.8	6.5	13.2	3.5
Wool fibers treated ($KMnO_4$ content = 9%)	294.2	408.5	540.1	173.3	70.2	11.1	14.9	3.8
Original cashmere fibers	287	402	533.7	166.1	73.2	8.8	14.9	3.1
Cashmere fibers treated ($KMnO_4$ content = 9%)	289.6	404.6	536	169.4	71.2	10.6	14.7	3.5

ed ($KMnO_4$ content = 9%) disappears, compared with the original cashmere fibers. Thus the cashmere fibers treated are damaged when the $KMnO_4$ content is 9%. ***Figure 1.f*** also shows the degree of cashmere fiber damage.

X-ray diffraction

Based on the X-ray diffraction results of the fibers and ***Equation (4)*** & ***Equation (5)***, the crystallisation index (CI) and relative CI of the fibers are shown in ***Table 2***. Based on ***Table 2***, the CI of the original wool fibers is less than that of the original cashmere fibers. However, the CI of the wool fibers treated ($KMnO_4$ content = 9%) is more than that of the cashmere fibers treated($KMnO_4$ content = 9%). The relative CI of the wool fibers treated ($KMnO_4$ content = 9%) is twice as much as that of the cashmere fibers treated ($KMnO_4$ content = 9%). Hence the damage of wool fibers is less than that of cashmere fibers under potassium permanganate solution treatment conditions.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy results of the fibers are shown in ***Figure 3***. The element contents of the wool and cashmere fibers are shown in ***Table 3***. Compared with the original wool fiber, the C content of the wool fibers treated decreases, but the N, O, and S contents increase. The C content and O content of the cashmere fibers treated decrease, but the N content and S content increase, compared with the original cashmere fiber. The C content of the original wool fibers is higher than that of the original cashmere fibers. The C, N, O, and S contents of the wool fibers treated are almost the same as those of the cashmere fibers treated.

Conslusions

Both wool and cashmere fibers are of the animal natural protein type. However, the damage degree of cashmere fibers is

serious compared with wool fibers under the same potassium permanganate solution treatment conditions. When the potassium permanganate content is 9%, the scales of the cashmere fibers treated disappear, and the relative crystallisation index seriously decreases. Moreover the weight loss of the cashmere fibers treated is slightly bigger than that of the wool fibers treated when the potassium permanganate content is 9%. After that, the difference between the weight loss of the cashmere fibers treated and that of the wool fibers treated increases. The force loss of the cashmere fiber treated increases linearly with an increase in potassium permanganate content.

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