Effects of a Clean Subcritical Degreasing System on Wool Fibers

by

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Abstract

It makes sense to use environmentally friendly methods of degreasing in fur-making process. In this study, subcritical n-pentane was used to degrease wool fibers. Thermogravimetric analysis (TGA) was used to observe and analyze the properties of the subcritical n-pentane degreased wool fibers. The results showed that the thermal stability of the fibers increased. Fourier Transform Infrared (FTIR) spectroscopy was used to analyze the structural changes of macromolecular chains in wool fibers. It was found that when the pressure was higher than 0.4 MPa, the wool fibers underwent a conformational change with the α-helix changing to β-folding. If the pressure was as high as 0.6 MPa, the disulfide bonds in the wool fibers scale layer appeared to break. X-ray powder diffraction experiment was used to study changes in wool fiber aggregation morphology. It was demonstrated that the crystalline zone of wool fibers changed and the fibers index grew, from 22.89% to 30.19%. Field emission scanning electron microscopy and ultra-depth of field microscopy was used to analyze changes in the surface morphology of wool fibers. The results suggested that after the treatment, the wool fibers were not damaged and the impurities on the wool surface were reduced.

Introduction

As we all know, fur is famous for its nobility and elegance, as well as its beautiful appearance. Sheep furs and otter furs are popular with consumers for their relatively low price and excellent warmth. Wool and its products have the following characteristics: practicality, beauty, luxury, value preservation, and sensitivity. In the production of leather, the wools are treated as superfluous and are often removed, resulting in solid waste.[1] However, the removed wool fibers occupy a crucial position in the consumer market. For example, rabbit wools and sheep wools, which are important raw materials for clothing products, are often mixed with man-made fibers and woven into sweaters, where the incorporation of animal wool gives the sweater softness, warmth and lightness. In fact, whether it is rabbit wool or sheep wool, its external structure is a dense layer of scales.[2] The keratinized cells that make up the scales are arranged in a certain order, forming a dense and strong protective layer on the outside of the wool.[3] Due to the presence of the scales, it is difficult for most foreign substances to enter the interior of the wool, thus it retains good physical and chemical properties such as thermal stability and crystallinity.[4] In order to satisfy the aesthetics of public consumption, to give the fur products a good feel and to enhance the value of the fur products, large amounts of water is used as a medium to dissolve large amounts of chemical reagents in the fur production process. Wool production wastewater is large in volume, with many types of pollutants, complex composition, high concentration, high chromaticity, and difficult to treat.[5] In the degreasing process, many degreasers are added to the bath in order to remove excess oil from the wool. These degreasers, which contain high levels of surfactants, are difficult to handle and pose a threat to the environment when discharged into waste water.

Cleaner production is one of the most effective ways to tackle pollution in wool processing. Through the transformation of the wool process, the amount of effluent generated during the production process is reduced at the source. This reduces the investment and running costs of end-of-pipe treatment facilities and eliminates or reduces the risk of products being taken off the market due to environmental problems. At present, subcritical fluid technology has been widely used in the field of cleaner production, such as functional and medicinal plant extraction and production,[6,7] plant essential oil extraction and production,[8,9] edible oil extraction and production,[10,11] plant pigment extraction and production,[12,13] tobacco industry,[14,15] textile industry[16,17] and other industries. The advantages of subcritical extraction processes are as follows. Firstly, the solvent is basically not left behind in the product. Secondly, it does not cause damage to heat-sensitive components in the material. Finally, compared to supercritical extraction technology, large-scale production has been achieved with low investment and low production costs, with the daily processing of 30t of complete sets of equipment only more than 2 million yuan.[18] A few people combine subcritical solvent with wool production and processing. If subcritical fluid can be applied to fur production to replace water as a clean solvent, the wastewater generated in fur production will be greatly reduced.

In a previous paper,[19] subcritical n-pentane was used to degrease sheepskin and its effect on sheepskin was investigated. The results showed that it can remove grease from adipose glands and hair

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follicles and it is a clean and efficient degreasing method. So, on this basis, the effect on the wool by subcritical solvent degreasing system was studied further. The degreasing rate of subcritical system applied to wool and the effects of subcritical system on wool thermal stability, aggregation morphology, macromolecular chain structure and surface morphology were mainly studied. It provides feasibility for cleaner production in fur industry.

Experimental

Materials

N-pentane was purchased from Fuchen (Tianjin) Chemical Reagent Co., Ltd. While potassium bromide and alcohol were purchased from Chengdu Changlian Chemical Reagent Co., Ltd. Sheep wool fibers are native of Chengdu.

Sample Preparation

After soaking, flesh was removed from the skin and then the wool was cut off and frozen. Each test consisted of 10g of wool.

The Experimental Process

According to the previous research, it is known that degreasing pressure has a significant influence on the degreasing effect of subcritical n-pentane.[19] Therefore, in these experiments of treating sheep wool fibers with subcritical n-pentane, a representative process condition (degreasing pressure) was selected as a single factor variable. Five different pressures were designed in the experiment: 0.2, 0.3, 0.4, 0.5 and 0.6 MPa. Other degreasing process parameters were as follows: degreasing time 60 min, degreasing temperature 40.5°C, material-liquid ratio 1:7.

The experiment was conducted in a magnetically coupled reactor shown in Figure 1.

Characterization Techniques

Degreasing rate

The degreasing rate was calculated by the following formula:

Where Y is degreasing rate, X_0 represents the oil content of wool fibers before degreasing and X_1 represents the content of removed degrease. X_0 is determined by the difference of the mass before and after degreasing. X_1 is determined by Soxhlet extraction.[20]

$$Y = X_0 / X_1 \times 100\%$$

Change in Thermal Stability in Wool

About 5g samples were weighed and placed in thermogravimetric analyzer (made in Switzerland) for the test at a temperature rise rate of 10°C/min under the condition of nitrogen protection and the temperature range was 150-600°C. During the experiment, the wool fibers were cut into smaller pieces, and then the crucible with wool fibers was put on the balance of the analyzer, and the weight loss of it with the increase of temperature observed. Thermogravimetric analysis (TGA) can accurately measure the process that the mass of the measured substance changes with the change of temperature or time, and is widely used in the research fields of inorganic materials, organic materials, medical drugs and so on.

Structural Changes in Wool Fibers Macromolecular Chains using Fourier Transform Infrared (FTIR) Spectroscopy

In this experiment, the detection parameters of Fourier transform infrared spectrum were as follows: the detection range 4000-400cm, the wave number accuracy 0.01cm, the resolution 0.09cm, the linearity less than 0.07%, and the peak-to-peak noise value better than 5000:1[-1]. Before analysis and determination, the wool fiber samples were cut into pieces and ground together with potassium

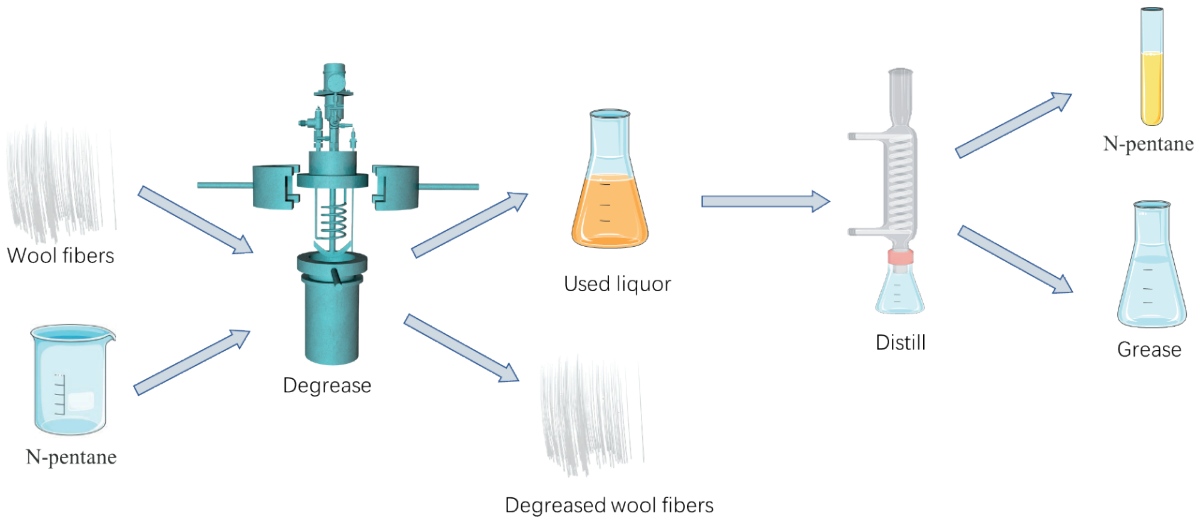

Figure 1. The wool fibers degreasing procedure with subcritical n-pentane.

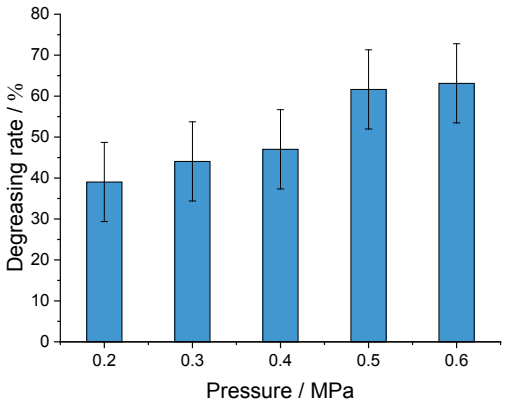

Figure 2. Degreasing rate at different pressures.

bromide powder under the irradiation of a Nernst lamp. After full grinding, the mixture of wool fibers and potassium bromide powder was tabletted, and finally put into a Fourier transform infrared spectrometer for determination.

Structural Changes in the Aggregation State of Wool Fibers ssing X-Ray Powder Diffraction

X-ray crystallographic analysis was performed on an AXIS Ultra DLD diffractometer (made in The United Kingdom), coupled to a Cu lamp (λ = 1.5405 Å). The scanning range 5.015-50.000, step size of 0.026° with continuous scanning.

Morphological Changes on the Wool Surface using Scanning Electron Microscopy and Ultra-Depth Microscopy

Field emission scanning electron microscopy (FE-SEM) measurements was performed using a JSM-7500F (made in Japan) instrument. FE-SEM is a widely used analytical instrument, which can explore the surface changes of wool fibers. In the process of experiment, wool fibers were dried by vacuum dryer for 24 h, then gold-plated. Super-depth microscopic observation was carried out on a VHX-700FC Depth-of-field microscope (made in China).

Results and discussion

Effect of Degreasing

As can be seen from Fig. 2, the degreasing rate of subcritical n-pentane increases with the increase of degreasing pressure. When the degreasing pressure increases from 0.4 MPa to 0.5 MPa, the degreasing rate of subcritical n-pentane improves significantly.

Effect of Subcritical n-Pentane Treatment on Thermal Stability of Wool Fibers

In order to study the influence of subcritical n-pentane on wool fibers, the wool fibers treated with subcritical n-pentane under different pressures were subjected to thermogravimetric analysis with the test temperature ranging from 150°C to 600°C, and the obtained thermogravimetric analysis curves are shown in Fig. 3. The point identified in the figure is the inflection point of weightlessness.

It can be seen from Fig. 3 that the TG curves of wool fibers in the control group and the experimental group can be divided into three stages. In the temperature range from 150°C to 250°C, the weightlessness is mainly due to the volatilization of moisture, perspiration and other components in the wool fibers. During the temperature range from 250°C to 400°C, the weightlessness is mainly attributed to breakage of hydrogen and disulfide bonds in the peptide chain which produces some volatile gases such as H_2S, SO_2 and CO_2. When the temperature rises above 400°C, the weightlessness is due to the decomposition and consumption of residual carbonized substances in wool fibers.[21] It can be seen that the inflection point of weightlessness of the treated sample is increased compared with the

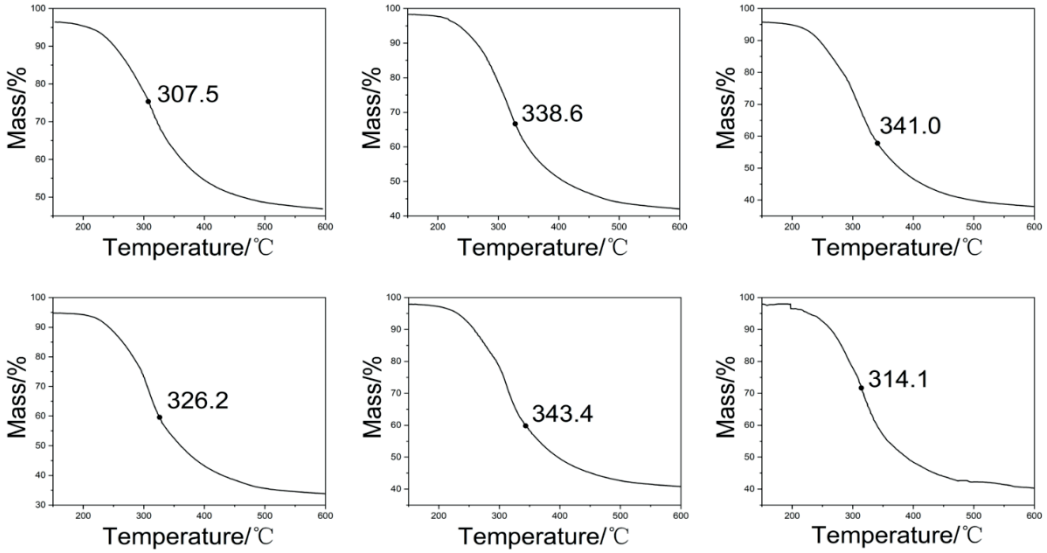

Figure 3. TG analysis curves of wool fibers under different pressures (**a**, **b**, **c**, **d**, **e** and **f** is blank sample, 0.2Mpa, 0.3Mpa, 0.4Mpa, 0.5Mpa and 0.6Mpa).

blank sample. The thermal stability of wool fibers is enhanced after treatment with subcritical n-pentane.

Effect of Subcritical n-Pentane Treatment on Macromolecular Chain Structure of Wool Fibers

In order to explore whether subcritical solvent will affect the interaction between macromolecular segments and the stability of functional groups of wool fibers. Wool fibers treated with subcritical n-pentane under different pressures were selected for Fourier Transform Infrared Spectroscopy (FT-IR) analysis. The abscissa of FT-IR analysis chart is wavenumber, and the ordinate is transmittance T. The formula of light transmittance T is:

$$T = I / I_0 \times 100\%$$

Where I and I_0 are the light intensity of infrared light passing through wool fibers and the light intensity passing through background.

Table I shows the characteristic infrared absorption band of wool fibers. In order to compare the intensity changes of characteristic peaks, several main characteristic peaks were normalized based on the absorption peak (C-H) at 2990 cm^{-1}. Table II shows the relative intensity of each characteristic peak after normalization.

Table I

Infrared characteristic absorption band of wool fibers22

Category	Wavenumber / cm^{-1}	Vibration mode
Hydrogen bond	3300-3500	NH Contraction and Amide II Resonance Absorption
Amide I	1600-1685	C=O stretching region
Amide II	1480-1575	CN and NH stretching
Amide III	1229-1301	CN and NH stretching
Amide IV	625-767	OCN and other kind of stretching

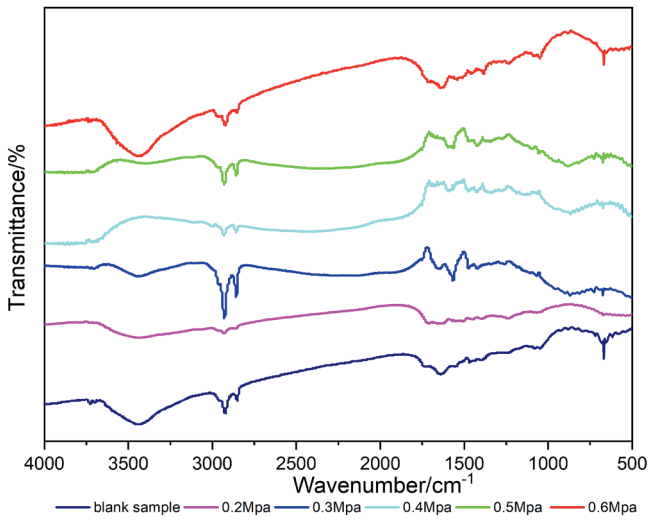

Figure 4. FT-IR analysis of wool fibers at different pressure.

Table II

Relative intensity of some characteristic peaks of wool fibers after subcritical n-pentane treatment at different pressure

Pressure/ MPa	I_{2840} / I_{2990}	I_{1640} / I_{2990}	I_{1240} / I_{2990}	I_{1050} / I_{2990}
Blank sample	1.007	1.040	1.085	1.098
0.2	1.005	1.014	1.030	1.047
0.3	1.002	1.006	1.023	0.990
0.4	1.000	1.018	1.109	1.093
0.5	1.000	1.031	1.087	1.024
0.6	1.010	1.028	1.101	1.112

Figure 4 shows the infrared spectra of wool fibers treated with subcritical n-pentane under different pressures. Table II shows the relative strength values of each characteristic peak of subcritical wool fibers after normalization. It can be found from Fig. 4 and Table II that the relative intensity of Amide I (C = O) characteristic peak at 1640 cm^{-1} of wool fibers decreased from 1.040 (blank sample) to 1.014 (0.2MPa), 1.006 (0.3MPa), 1.018 (0.4MPa), 1.031 (0.5MPa) and 1.028 (0.6MPa). The results indicated that the effect of C=O bond related to α -helix conformation in wool fibers treated with subcritical n-pentane was weakened. After being treated with subcritical n-pentane at 0.4, 0.5 and 0.6MPa, the relative intensity of Amide III (CN, NH) characteristic peaks at 1240 cm^{-1} of wool fibers increased from 1.085 (blank sample) to 1.109, 1.087 and 1.101 respectively. However, after 0.2 MPa and 0.3MPa subcritical n-pentane treatment, the relative intensity of Amide III (CN, NH) characteristic peaks at 1240 cm^{-1} of wool fibers showed a weakening trend, which decreased to 1.030 and 1.023 respectively. The results indicated that Amide III with β-folding conformation in wool fibers decreased after 0.2 MPa and 0.3MPa subcritical n-pentane treatment, while Amide III with β-folding conformation in wool fibers increased after 0.4 MPa, 0.5 MPa and 0.6MPa subcritical n-pentane treatment. It can be seen that the molecular chain structure of wool fibers changes from α-helix to β-folding after being treated with subcritical n-pentane higher than 0.4MPa. The structural changes are shown in Fig. 5. However, when the treatment pressure is less than 0.4MPa, the molecular chain structure of wool fibers does not change obviously.

At the same time, it can be seen from Table II that the relative intensity of the characteristic peak of S-O in cystine oxide of wool fibers at 1050 cm^{-1} increases from 1.098 (blank sample) to 1.112 (0.6MPa). The related characteristic peak of 2840 cm^{-1} C-H also increased from 1.007 (blank sample) to 1.010 (0.6MPa). It can be seen that when the treatment temperature is as high as 0.6MPa, disulfide bonds in wool fiber scales break and the polarity around -CH_2- group is enhanced.

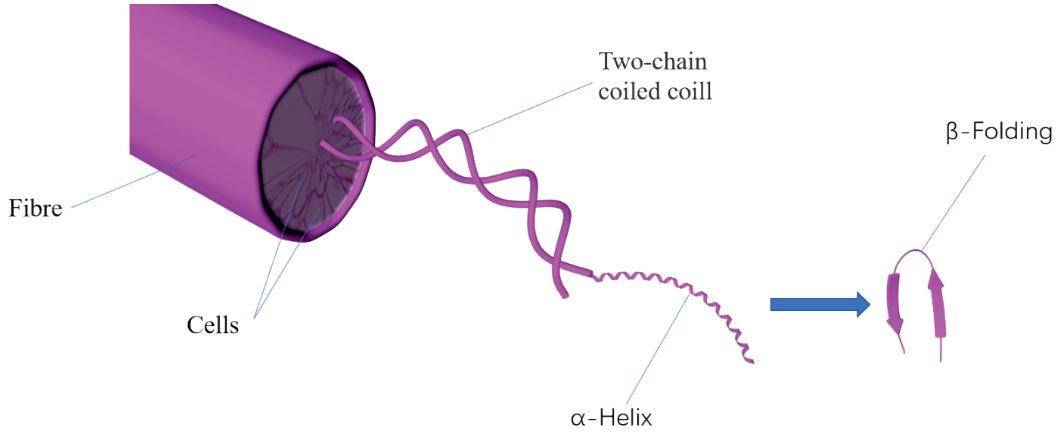

Figure 5. Structural changes of wool fibers.

Effect of Subcritical N-Pentane Treatment on Aggregate Structure of Wool Fibers

In order to analyze the effect of subcritical n-pentane treatment on the aggregated structure (such as crystalline structure and amorphous structure) of wool fibers, wool fibers treated with 0.5 MPa subcritical n-pentane are selected for X-ray powder diffraction analysis. The abscissa of X-ray powder diffraction pattern is diffraction angle 2θ, and the ordinate is diffraction intensity I. The formula of crystallinity C.I. is:

$$C.I.\,(\%) = I_{9^\circ} - I_{14^\circ} / I_{9^\circ} \times 100\%$$

Where I_{9° and I_{14° are the maximum diffraction intensities of diffraction peaks with diffraction angles 2θ around 9° and 14°23.

Fig. 6 describes the X-ray powder diffraction patterns of wool fibers treated at different conditions. It can be seen from Fig. 6 that there

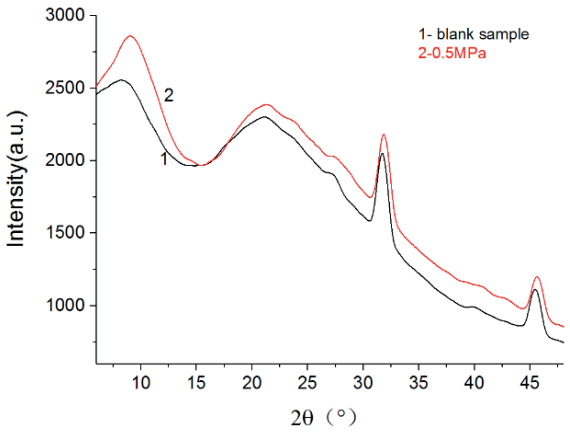

Figure 6. X-ray powder diffraction analysis of wool fibers under different conditions.

are very obvious diffraction peaks near the diffraction angles 2θ of 9° and 20°, which are the common diffraction peaks of α-crystal and β-crystal in wool fibers. Compared with blank samples, the diffraction peak strength of wool fibers treated with 0.5MPa subcritical n-pentane increased at 9° and 20°, and the width of the diffraction peak also widens. The results indicate that the crystal form of the crystalline region of wool fibers changed after 0.5MPa subcritical n-pentane treatment, and the α-crystal changed into β-crystal.

Table III shows the change of crystallization index of wool fibers after treatment under different conditions. It can be seen from Table III that the crystallization index of wool fibers increased from 22.89% to 30.19%. Therefore, after treatment with subcritical n-pentane, the α-crystal and β-crystal crystallization in wool fibers increased and the crystallinity of wool fibers significantly improved.

Table III

Crystallization index of wool fibers under different conditions

Condition	$I_{9.0^\circ}$	$I_{14.1^\circ}$	C.I.
Blank sample	2534	1954	22.89%
0.5 MPa	2875	2007	30.19%

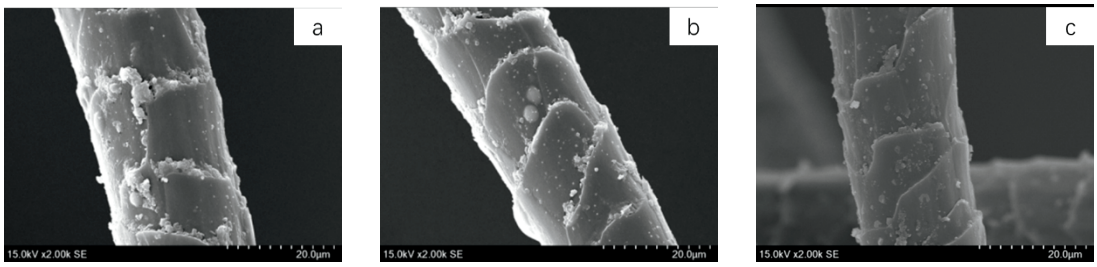

Figure 7. SEM micrographs of wool fibers under different pressures (**a**, **b** and **c** represent wool fibers before treatment, after 0.2 MPa subcritical n-pentane and 0.6 MPa subcritical n-pentane).

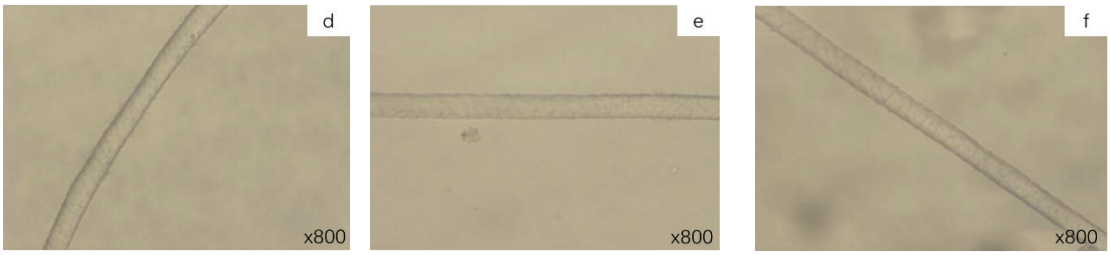

Figure 8. VHX micrographs of wool fibers under different pressures (**d**, **e** and **f** represent wool fibers before treatment, after 0.2 MPa subcritical n-pentane treatment and 0.6 MPa subcritical n-pentane)

Effect of Subcritical N-Pentane Treatment on Wool Surface Morphology

In order to investigate the effect of subcritical n-pentane on the surface morphology of wool fibers, wool fibers treated with 0.2 and 0.6 MPa subcritical n-pentane are selected for scanning electron microscope and super depth of field microscope. The observation results are shown in Fig. 7 and Fig. 8.

It can be seen from Fig. 7 and Fig. 8 that the scales covered by wool fibers before treatment are thick, arranged and complete in shape. Some impurities are attached to the scales. It can be seen from the graph that the subcritical treatment did not cause significant damage to the wool fibers. However, the impurities on the wool fibers were decreased, indicating that subcritical n-pentane can remove the impurities from the wool surface.

Conclusion

The results show that subcritical n-pentane is an environmentally viable degreaser and the degreasing rate increases with increasing pressure. After subcritical n-pentane treatment, wool fibers showed the following changes: The thermal stability of wool fibers improved. If the pressure was higher than 0.4 MPa, the wool fibers underwent a conformational change from the α-helix to β-folding. When the pressure reached 0.6 MPa, the disulfide bond broke. After 0.5 MPa of subcritical n-pentane treatment, the crystallization pattern of wool fibers crystallization zone changed from α-crystal to β-crystal, and the crystallization index increased from 22.89% to 30.19%. The subcritical treatment does not damage the wool and also removes impurities from the surface of the wool.

Acknowledgement

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