Study on the Dry-Cleaning Process of Mink Fur Based on Subcritical Solvent

by

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Abstract

It is significant to apply environmentally benign technology to fur processing. In this paper, subcritical extraction with n-pentane was used to dry clean mink fur and the effect on the quality of mink fur was studied. The dispersion degree of the leather fibers and the morphology of the wool fiber were characterized with SEM, the mechanical properties, shrinkage temperature and oil content left in fur were determined and analyzed. The results showed that the fibers of mink fur were well separated and no excess lipids in the fibers or on the surface of mink fur and the hair of the mink fur is not damaged. The tensile strength and elongation of mink fur show slight increase respectively, and the shrinkage temperature of mink fur that was treated by subcritical solvent was significantly increased compared with that of the mink fur treated with tetrachloroethylene by conventional dry cleaning method.

Introduction

Mink skin is one of the most important fur industry resources in the world because of its beautiful appearance, soft and firm of leather, dense villus and glossy aciulum (guard hair), which it is the ideal fur product for fur clothing. It is estimated that the global quantity of mink skin will exceed 30 million pieces in 2021.

The current tanning process of mink mainly includes soaking, degreasing, softening, pickling, aluminum tanning, kicking (oil tanning), dry cleaning, etc.[1] In the kicking operation, it is to smear the kicking oil on the flesh side of alum-tanned mink fur, and then to put the skin into the kicking machine for processing. The oil penetrates into the leather and is well distributed among fibers but the excess grease is attached on the kicked mink fur. The following step, named dry cleaning, removes the excess grease and provides the softness and extensibility of mink fur.

Because of the large amount of grease in the kicked mink fur, the conventional chemical emulsification method could not remove the excess kick oil effectively. Solvent extraction with tetrachloroethylene or trichloroethylene is usually used to dry clean the kicked mink fur to remove excess kick oil. During the dry cleaning process, a common solvent (tetrachloroethylene) is used in closed-circuit machines, then centrifugating and drying (36-38°C), finally tetrachloroethylene is recovered as far as possible for reuse but some is left in mink fur. Because tetrachloroethylene is a harmful organic solvent which has the phenomenon of irritation and anesthetic effect, it must be removed from the cleaned fur after dry cleaning. However, due to the higher boiling point, tetrachloroethylene is hard to remove. Thus, harmful residues could cause air and water environment pollution.[2,3] According to the factory's statistics, each mink skin consumes about 15g, and the residual solvent in the skin will eventually evaporate into the air and cause air pollution. In order to solve this problem, Marsal et al.[4,5] studied the degreasing process of leather with supercritical CO_2, and the degreasing efficiency was as high as 94%. However, this is of no practical significance for fur degreasing due to equipment input and cumbersome operation. Bufalo et al.[6] studied the ultrasonic-assisted degreasing of mink skin in water system, which can effectively avoid the use of harmful substances and the discharge of degreasing waste liquid. Zhang et al.[7] put forward a concept of green controllable solvent for fur degreasing.

Subcritical extraction is a new technology developed within the past 20 years. It is a subcritical solvent extraction of lipids from biological materials.[8] When the temperature of a substance is above its boiling point but below its critical temperature, and the pressure of a substance is below its critical pressure, the state of a substance in the form of a fluid is said to be subcritical.[9,10] When a solvent is in a subcritical state, we call it a subcritical solvent. For a solvent in a subcritical state, its density is similar to that of a liquid, the viscosity and surface tension of the molecule may change, its viscosity is similar to that of a gas, the mass transfer speed becomes faster, the diffusion ability becomes stronger, and it will have more significant dissolution ability and dispersibility for some substances.[11,12]

According to the comparison and evaluation of the properties and environmental effects of various solvents, n-pentane has a low boiling point and small required subcritical pressure, making it favorable for transportation and use at room temperature. In addition, n-pentane

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has the characteristics of easy to recover, no physiological toxicity and stable chemical properties.[13]

In this paper, n-pentane was selected as the solvent to dry clean minks under a subcritical system. Compared with tetrachloroethylene, n-pentane has a low boiling point and small required subcritical pressure. It is easy to recover the solvent after dry cleaning and has low toxicity. The mechanical properties and moisture and heat resistance of mink skin after being treated with subcritical n-pentane dry cleaning were tested and determined, fiber dispersion and wool scale were observed and analyzed, which provided inspiration and scientific basis for the application of subcritical technology in fur production and processing, so as to promote cleaner production of fine fur.

Experiment

Device and instruments

Reaction kettle: Subcritical dry cleaning was performed in a high pressure reaction kettle (GSH-1/10-SJFZ magnetic coupling reaction kettle) to facilitate the control of temperature and pressure in the subcritical system, as schematically illustrated in Figure 1.

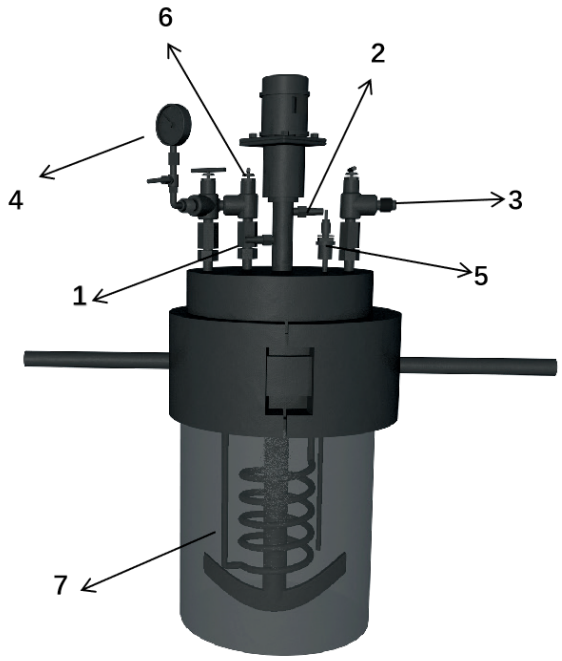


Figure 1. Reaction kettle for subcritical dry cleaning experiment.
(1) Circulation water inlet valve; **(2)** Circulating water outlet valve; **(3)** Inlet valve; **(4)** Piezometer; **(5)** Temperature probe; **(6)** Pressure valve; **(7)** Constant temperature circulating water

Scanning Electron Microscope (JSM-7500F) is used to observe mink fur samples to characterize the separation of fibers and the quality of the hair. Electronic tension machine (AI-7000) and leather shrinkage temperature test machine (HY-852) were used to determine the mechanical properties of the leather and hydrothermal stability, Moisture (YLS16A) meter to determine the moisture content, and automatic grease tester (SZC-101) to measure the grease content.

Materials and reagent

N-pentane: analytical reagent, purchased from Chengdu Jingsan Reagent Co. The critical temperature of n-pentane is 196.6°C. The critical pressure is 3.37 MPa and the boiling point of n-pentane is 36.1°C. The saturated vapor pressure is 121.48 kPa (38.5°C).

The raw material of mink fur was pastel mink imported from Denmark.

Methodology

Aluminum-oil tanning of mink fur

The aluminum-oil tanned mink fur was prepared by Sichuan Dehua Leather Co., Ltd. according to the existing mink fur processing. The processing process was as follows: soaking - softening - soaking - pickling - alum tanning - drying - smearing - kicking.

Control: The controlled sample was the mink skin tanned and kicked by process above, which was carried out in the dry cleaning machine with tetrachloroethylene for 5 minutes.

Subcritical n-pentane dry cleaning experiment

Two pieces of kicked mink furs (10×10cm each) were sampled. A quantity of n-pentane 30 times the mass of the sample was added to the kettle and preheated to 30°C, then the sample was put into the kettle. The closed reaction kettle was heated to the temperature of 40°C and pressure was increased to 0.5 MPa through compressed air at once. The dry cleaning duration is 3min and 1.5min respectively, as S1 and S2.

Shrinkage temperature

The Shrinkage temperature of mink fur was measured according to IULTCS/IUP 16, 2015. Each sample was measured three times and the average value taken.

Determination of fat content

First, the samples were dried with a moisture tester and the moisture content was measured. Then, according to the instructions of automatic fat tester (SZC-101), the fat content was measured with dichloromethane as the solvent. Each sample was measured twice and the average value taken.

Physical-mechanical tests

The tensile strength and percentage elongation of mink fur samples were determined according to the standard IULTCS (International Union of Leather and Chemists Association) methods. Tensile strength and percentage extension were measured according to IULTCS/IUP 6, 2011.

Morphological analyses

The longitudinal section of leather, over hair and wool of the samples were sprayed with gold respectively. Scanning Electron Microscope (SEM) was employed for the morphological characterization of fiber tissue dispersion and aciulum and villi.

Results and discussion

In a subcritical system, dry cleaning was carried out in a confined space with organic solvents using the principle of organic similarity and compatibility. The dry cleaning agent was separated from the mink fur by vacuum evaporation to obtain the mink fur after eluting oil. The gaseous dry cleaning agent was reused after condensation.

Influence on hydrothermal stability

Shrinkage temperature (T_s) of the fur is used to characterize the effectiveness of tanning, and it is closely related to the hydrothermal stability of the fur. The results of the furs are seen in Table I.

As can be seen from Table I, T_s of the kicked mink fur is 58.1°C, but T_s of mink fur treated with subcritical n-pentane and conventional dry cleaning were significantly decreased due to detanning in dry cleaning process. T_s of S1 is about 20°C higher than that of control which shows the better hydrothermal stability. This means that the mink fur dry-cleaned by subcritical n-pentane has better hydrothermal stability and durability.

Moisture and fat content

It can be seen from Table II that the fat content of S1 and S2 by subcritical n-pentane or conventional dry cleaning were low, indicating that the kick oil absorbed during oil tanning and the nature oil in raw skin were mostly washed out. Degreasing rate are 92.72%, 88.93% and 88.12% compared with the kicked fur. Although the fat content of the samples was higher than that of the control, this may be related to the type of solvent and degreasing time.

Influence on mechanical strength of leather

As can be seen from Table III, compared with the traditional dry cleaning process, the tensile strength and elongation of the mink fur treated by the subcritical n-pentane were both improved by 17.08% and 13.09% in S1, while the difference was not significant in S2. It is shown that the tensile strength and elongation would decrease along with extension of dry cleaning time.

Table I

Shrinkage temperature

Sample	Kicked fur	Control	S1	S2
Shrinkage temperature/°C	58.1±0.2	30.8±1.0	51.2±0.4	49.1±0.3

Table II

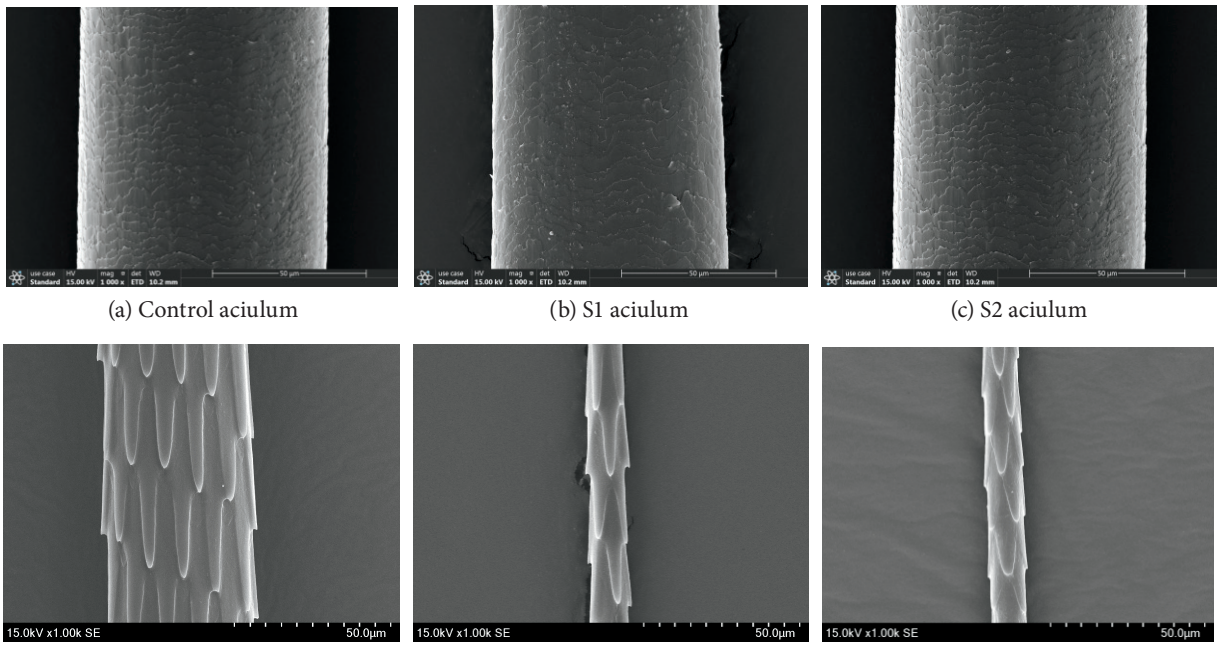
Moisture and fat content

Sample	Kicked fur	Control	S1	S2
Moisture content (%)	5.23	10.82	9.90	11.07
Fat content (%)	46.98±0.35	3.42±0.24	5.20±0.68	5.58±0.44

Table III

Mechanical properties

Sample	Thickness (mm)	Tensile strength (MPa)	Elongation (%)	Specify the load Elongation (5N/mm²)
Control	0.45±0.01	16.80±0.09	51.2±0.7	31.3±0.7
S1	0.44±0.02	19.67±0.10	57.9±0.6	31.7±0.1
S2	0.45±0.02	22.56±0.14	52.7±0.1	29.5±0.2



(a) Control aciulum (b) S1 aciulum (c) S2 aciulum

(d) Control villi (e) S1 villi (f) S2 villi

Figure 2. SEM of aciulum and villi

Influence on wool fiber

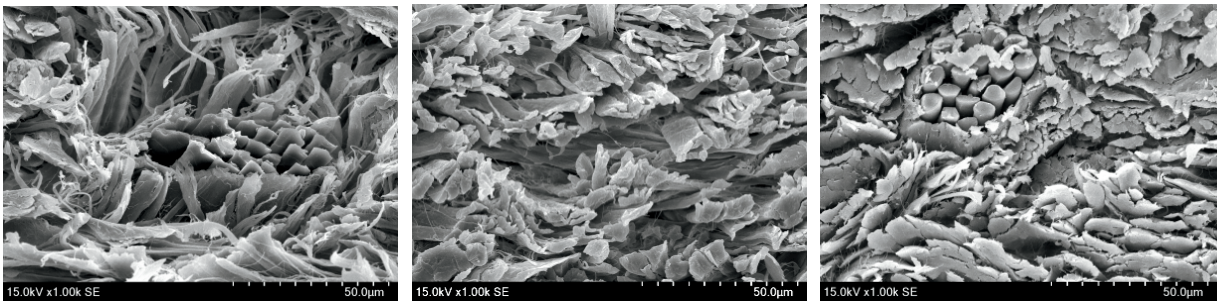
The hair is composed of the scales (cuticula), cortex, and medulla layers. The scales layer is a characteristic surface structure of the hair fiber, which is composed of flaky keratinocytes.[14] Its main function is to protect the hair fibers from the chemical and physical effects of the environment, giving the hair a glossy appearance.

Figure 2 shows the SEM image (X1000) of aciulum and villi respectively. The wool of mink is divided into aciulum and villi. Under the electron microscopy, the aciulum scales are arranged in a hybrid waveform, while the villus scales are arranged in a long petal shape. The structure of aciulum, villi scale layer and leather of mink dry cleaned by subcritical n-pentane showed no significant difference from that treated by traditional dry cleaning technology. The hair fibers were bright, flexible, uniform and even. The structure of hair fiber scale layer was complete, closely arranged and connected with each other.

Influence on leather

The tissue structure of mink fur is composed of three layers of epidermis, dermis and subcutaneous tissue. The characteristics of the tissue structure of the leather are dense collagenous fiber braiding, thin fiber bundles in papillary layer and tightly woven in cross shape, and thick fiber bundles in reticular layer, mainly parallel to skin surface.[15]

Figure 3 shows the SEM image (X1000) of the longitudinal section of the mink fur. It can be observed that after the subcritical n-pentane dry cleaning, most of the oil of mink fur was removed, the inter fibrillar substance was also dissolved. This makes the fiber bundles direction clearer, the collagen fiber bundles well dispersed, the fur firm and thin, soft feel, with good sensory performance.



(h) Control (i) S1 (g) S2

Figure 3. SEM of mink skin

Conclusion

The subcritical fluid has the characteristics of both liquid and gas, low viscosity, easy diffusion and strong solubility, etc. In this paper, the dry cleaning and degreasing process of mink fur with subcritical n-pentane was studied and the results were compared with those of conventional dry cleaning.

(1) The hydrothermal stability analysis shows that the shrinkage temperature of mink fur after dry cleaning with subcritical fluid is increased, which is beneficial to improve the hydrothermal stability and durability.

(2) The analysis of intradermal oil content indicates that the subcritical fluid dry cleaning process can effectively remove the oil.

(3) The analysis of mechanical properties indicates that the tensile strength and elongation of mink fur are improved after dry cleaning with subcritical fluid.

(4) SEM shows that there are no excess lipids on the surface of the hair and scales treated with the subcritical fluid, the structure of the scales of aciulum and villi and the leather are basically consistent with that of the traditional dry-cleaning process, and the dry-cleaning effect is obvious.

Overall, mink dry cleaning process based the subcritical system can effectively reduce the use of harmful chemicals. And dry cleaning solvent can be recycled through condensation recovery, thus reducing production cost, effectively separating uncombined grease and utilizing wastes. This paper provides inspiration for the application of subcritical technology in fur production and processing, hoping to promote the development of clean and environmental protection of fur industry, improve economic benefits and promote the progress of society.

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