

Supercritical Carbon Dioxide-Assisted Loosening Preparation of Dry Leather

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ABSTRACT: The physical modification of the dry leather using supercritical carbon dioxide (SC-CO₂) was studied in this article. A series of loosening processes of the leather fibers were carried out by changing the experimental conditions such as experimental pressure, experimental temperature, and time. The samples were characterized by scanning electronic microscopy (SEM), Brunauer–Emmett–Teller (BET) and X-ray diffraction (XRD). SEM images show that samples were loosened by SC-CO₂ and the leather fibers in micron size arrange more orderly after treatment. The BET surface area of treated samples increase from 1.67 m²/g to 6.33 m²/g with the changing of conditions. The optimal

treatment conditions were determined. Moreover, XRD patterns indicate that aggregation structure of collagen fibers in the sample was altered by SC-CO₂, and it can be found that the loosening of leather mostly happened in amorphous regions of collagen fibers. Besides, the percent breaking elongation of the samples was examined by means of a tensile analyzing test, and it indicates that the elongation at break of all the treated samples in SC-CO₂ can increase to 128.2% compared with 95.9% of the original ones. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 4015–4022, 2009

Key words: looseness; leather fiber; supercritical CO₂

INTRODUCTION

The environmental impact of the tanning industry is generally significant with outputs of wastes, i.e. high concentrations of organics, salts, and heavy metals (chromium compounds), both in solid and liquid form.¹ For example, processing 1 ton of raw hide generates 200 kg of final leather product, 250 kg of nontanned solid waste, 200 kg of tanned waste, and 50,000 kg of wastewater.² Pollution from tanneries, as from any major industry, has a negative long-term impact on the growth potential of a country, irrespective of the immediate economic benefits of production. Thus, environmental challenges from leather processing arise from the nature and quantity of chemicals used as well as the amount of wastes generated and discharged.

To bring the tanning industry more in line with present environmental thinking, various methods have been devised to reduce impacts. The potential use of ultrasound in leather process industry with the aim to reduce pollution load, decrease process

time, and get improvement in the product quality were being studied extensively.^{3–6} Other methods^{7–9} of cleaner process in leather-making process are tested synchronously, such as an approach from hair burning to hair saving using a lime-free unhairing system to cleaner production. However, wastewater cannot be avoided in above methods.

A new clean technology of leather making, in which supercritical carbon dioxide (SC-CO₂) fluid replaced water, was developed. In this technology, sewages could be eliminated from the origin of the leather-making industry. Supercritical CO₂ has been employed in the degreasing of leather.^{10–14} The studies deal with the feasibility of the supercritical CO₂ extraction technology to degrease sheepskins. Thus, the need for organic environmentally damaging surfactants would be eliminated. Likewise, methods for the determination of pentachlorophenol¹⁵ in leather being based on supercritical fluid extraction with *in situ* acetylation are presented. Apart from these applications, supercritical CO₂ has been used for the determination of banned azo dyes in leather.^{16–19} It was showed that supercritical CO₂ can also be used in chrome tanning,²⁰ delimiting, enzymatic unhairing, bating, vegetable tanning, fat liquoring, and so on.^{21–23}

Loosening the leather fiber by supercritical CO₂ is the primary work in our study. As we known, the traditional loosening fibers process, leather liming (lime, sodium sulfide, etc.), is operated to achieve the objective of the leather loose fibers by means of decomposing the fiber in the high pH of the water

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environment. However, this process will produce high-pH value of sewage, which is rich in lime, sulfide, biology oxygen demand, chemical oxygen demand, lipidic saponification or emulsion matter, protein, hair degradation products, organic nitrogen, ammonia nitrogen salt, and so on. Especially for the lime used in this procedure, its large dosage and low solubility at room temperature contribute hugely to a great deal of solid sludge. Besides, both the deliming and softening processes will offer a lot of complicated sewage. But how about using (SC-CO₂) to take place of lime to loosen the leather fiber? So, in this article, systematic studies were done on the influence of condition parameters (such as pressure, temperature, and time) on the looseness of leather fiber, and thus, further study on microstructure of products has also been investigated. This method of loosening leather fiber in our experiment is a physical process, in which no chemical matter is produced and no excess decompose of fiber occurs, and it is hopeful to solve the environmental pollution problem.

EXPERIMENT

Materials

CO₂ with the purity of 99.9% was supplied by Zhengzhou Sanfa Gas Co. These materials were used without any further purification. Commercial dry sheepskin was obtained from the market.

Procedures

Dry sheepskins were dried at 313 K for 4 h in vacuum and then placed in a desiccator before use. Experiments were run in a 50 mL high-pressure stainless-steel vessel. A high-pressure syringe pump (Beijing Satellite Manufacturing Factory, DB-80) was used to charge CO₂ into the reaction vessel. A pressure gauge consisting of a transducer (IC Sensors Co., Model 93) and an indicator (Beijing Tianchen Automatic Instrument Factory, XS/A-1) with an accuracy of 0.01 MPa was connected to the vessel to determine *in situ* pressure change of the system. In a typical experiment, the vessel was placed into a constant-temperature controller. The closed reactor was heated in the temperature controller to a fixed temperature. Then dry sheepskin, in the form of strip (3 mm in length and 4 mm in breadth or shape made in term of standard ISO 3376-1976), was placed into the bottom of the steel vessel. Having been impregnated with CO₂, the cell was filled up to the desired pressure. At this desired pressure, the sample was exposed in (SC-CO₂) for a prescribed period of time. Finally, the valve of the reactor was opened and the pressure was quenched rapidly to

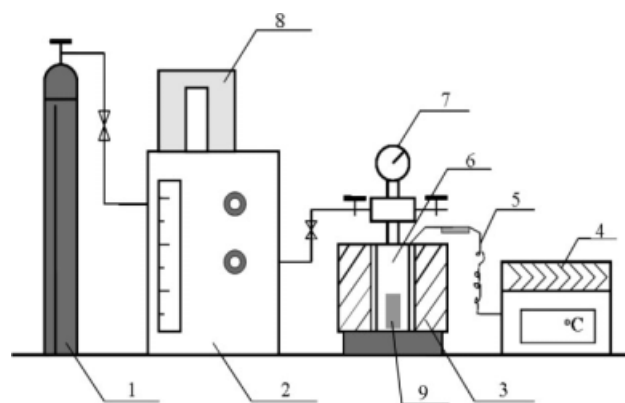


Figure 1 Schematic drawing of the experimental apparatus (1) CO₂ cylinder; (2) syringe pump; (3) heating jacket; (4) constant-temperature controller; (5) thermocouple; (6) vessel; (7) pressure gauge; (8) ice box; and (9) sample.

that of the atmosphere. The time of depressurization was around 6 s.

Using the supercritical CO₂ fluid technique, several variables can influence the loosening degree of sample: (a) temperature in range of 33–38°C; (b) pressure: the pressure of supercritical CO₂ during 8–16 MPa; (c) the time of constant pressure from 60 to 300 min. A schematic drawing of the apparatus is shown in Figure 1.

Characterization

The samples were studied using an AMRAY-1000B scanning electron microscope (SEM) at an accelerating voltage of 20 kV. The samples were prepared by sputter coating with gold forming a layer of approximately 100 Å in thickness. Nitrogen adsorption-desorption isotherms at 77 K were performed on a Quantachrome NOVA 1000e surface area and pore size analyzer. Before this measurement, the samples were heated at room temperature in 10⁻⁶ Torr nitrogen for 1.5 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the surface area. Tensile analyzing tests were conducted on a GMT5104 electronic universal machine to examine the elongation of the original or treated samples at temperature 20°C ± 2°C and humidity 65% ± 2%. X-ray diffraction data were recorded on a Rigaku D/MAX-3B using CuKα radiation at a scanning speed of 2° (2θ)/min within the 2θ range of 1.4°–70°.

RESULTS AND DISCUSSIONS

Effect of different experimental conditions on the structure of samples

A series of loosening processes of the leather fibers were carried out by changing the experimental

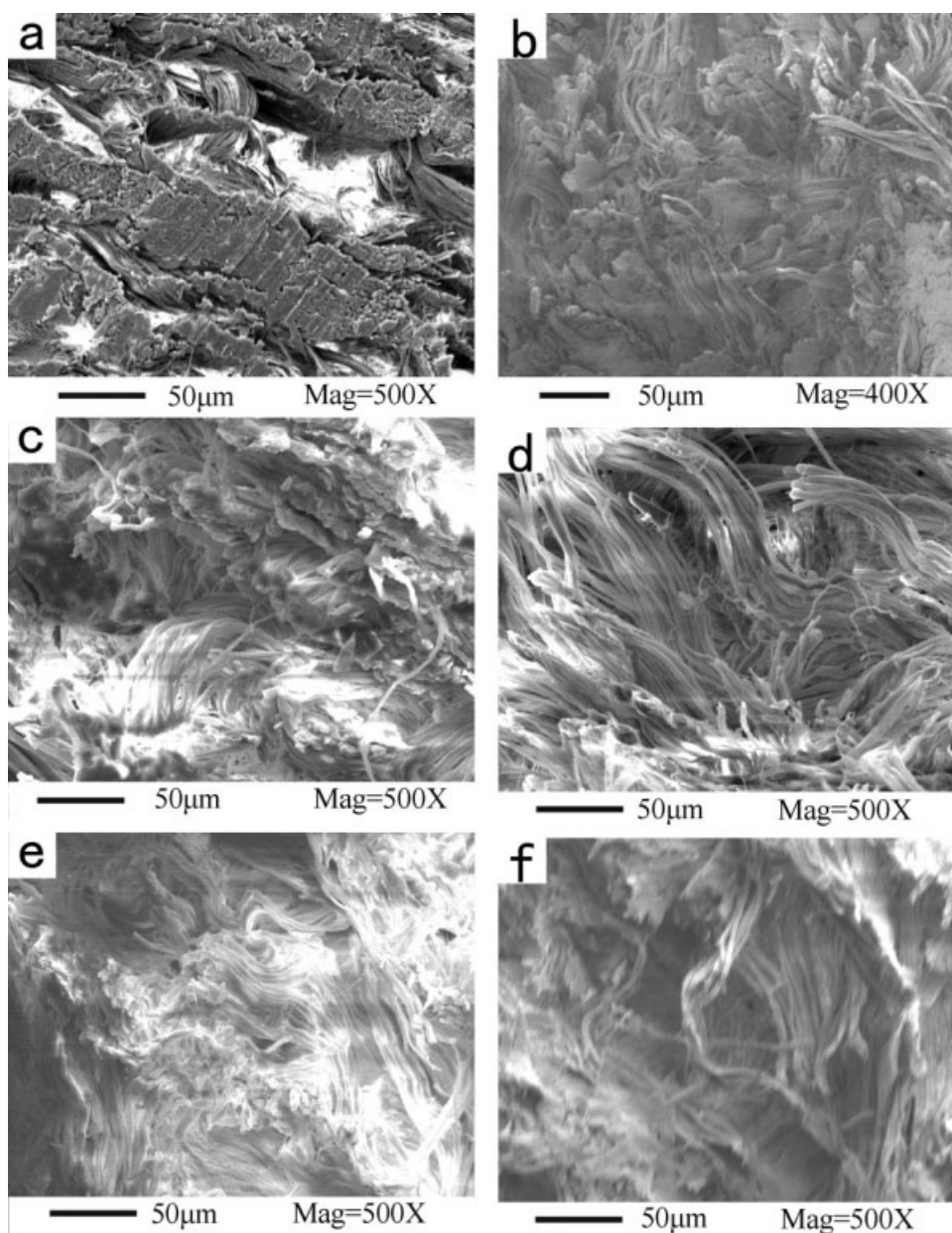


Figure 2 SEM images of the samples (side surface) treated at 38°C for 180 min under different pressures (a) untreated, (b) 8 MPa, (c) 10 MPa, (d) 12 MPa, (e) 14 MPa, and (f) 16 MPa.

conditions such as pressure, the time of keeping pressure and temperature. In addition, the influence of these variables on the structure of sample using the supercritical CO₂ technique was also discussed. In this article, we define the side remove from the chimera for inner surface of sheepskin and designate the contrary as outer surface. Also, the crosssection of the sheepskin was specified as side surface of the sample.

The effect of pressure on samples was studied at fixed temperature 38°C for 180 min. Observing the SEM images of the samples' side surface (Fig. 2) and inner surface (Fig. 3), it can be revealed that the distance between fibers first increase with pressure

until 12 MPa, usually for (SC-CO₂), when the pressure of SC-CO₂ increases, the density of SC-CO₂ also increases, leading to more CO₂ penetrating into collagen fibers, and the pressure releasing gradients is more evident while the vessel is depressurized. So, the aggregation structure of the sample could be altered, i.e. the distance between leather fibers will increase. Therefore, the degree of looseness in the samples increases with the increase of pressure from 8 to 12 MPa. Then, increasing the pressure of supercritical CO₂ beyond 16 MPa has no obvious effect on the looseness of samples. Hence, it is not necessary to increase the pressure excessively when this technology is applied in practice.

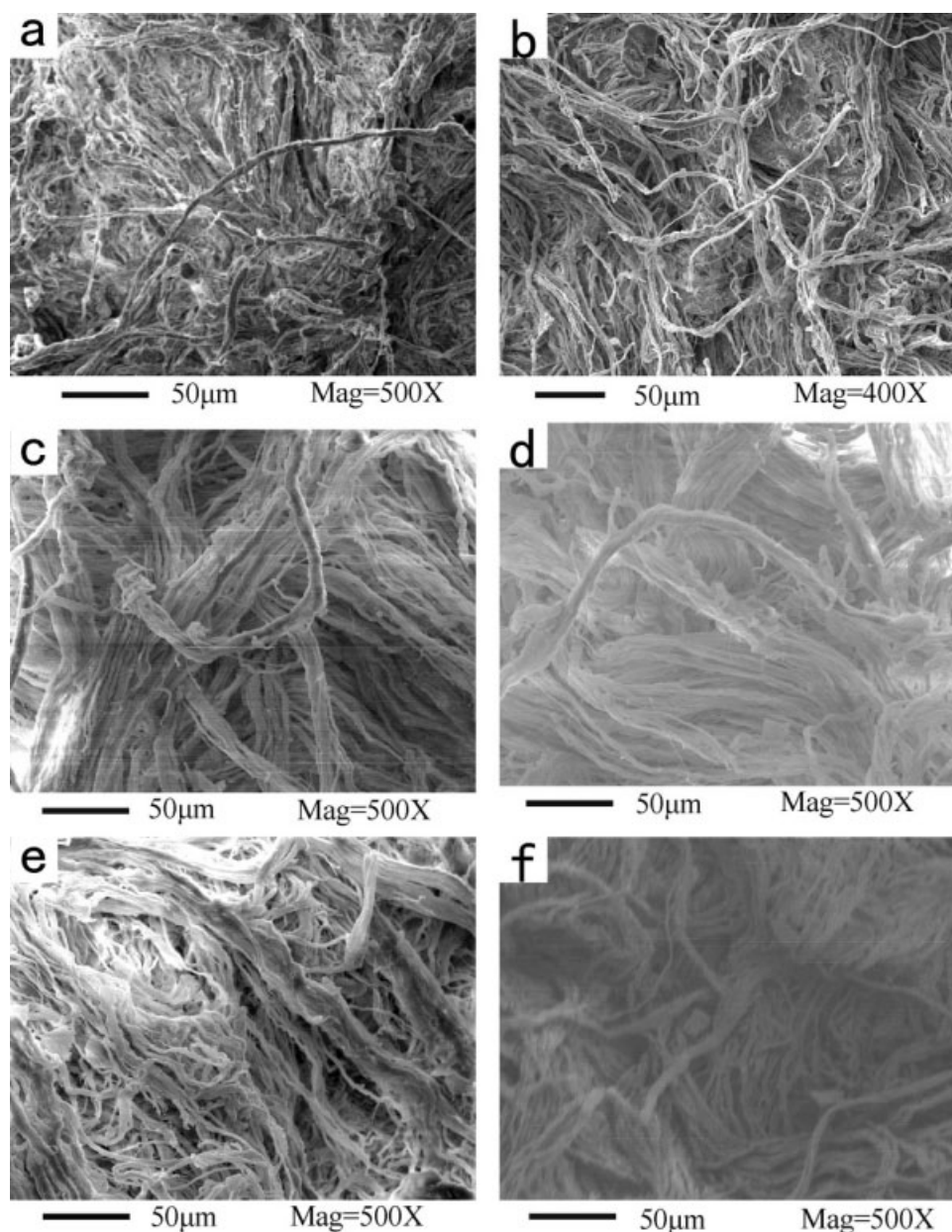


Figure 3 SEM images of the samples (inner surface) treated at 38°C for 180 min under different pressures (a) untreated, (b) 8 MPa, (c) 10 MPa, (d) 12 MPa, (e) 14 MPa, and (f) 16 MPa.

A series of experiments were also carried out at 12 MPa and 38°C to study the effect of time (within the range of 60–300 min) on the samples' structure. From the comparison of the SEM images in Figures 4 and 5, it can be shown that all the samples were loosened apparently by SC-CO₂, compared with the untreated sample [Fig. 2(a)]. However, there is a biggest looseness time condition of samples, i.e. when the time was fixed at 180 min, the effect of SC-CO₂ on the sample was the correspondingly best. At the same time, the leather fibers in micron size arrange more orderly after treatment by the impulsive force produced from rapid depressurization of SC-CO₂.

Likewise, the effect of treatment temperature by SC-CO₂ (within the range between 33°C and 43°C) on the microstructure of sheepskin samples was studied at the constant pressure 12 MPa for 180 min (Figs. 6 and 7). It is observed that the mean distance of fibers does not always increase with temperature. The existence of the optimal looseness of samples at 38°C is due to complex factors as: (1) the energy barrier for the motion units of collagen molecular chains decreased with the increase of temperature in supercritical CO₂; thus, it is easier for the motion of these units at higher temperature, and more interstices will be introduced. So, this factor is positive for the looseness of the sample; (2) usually for supercritical fluid,

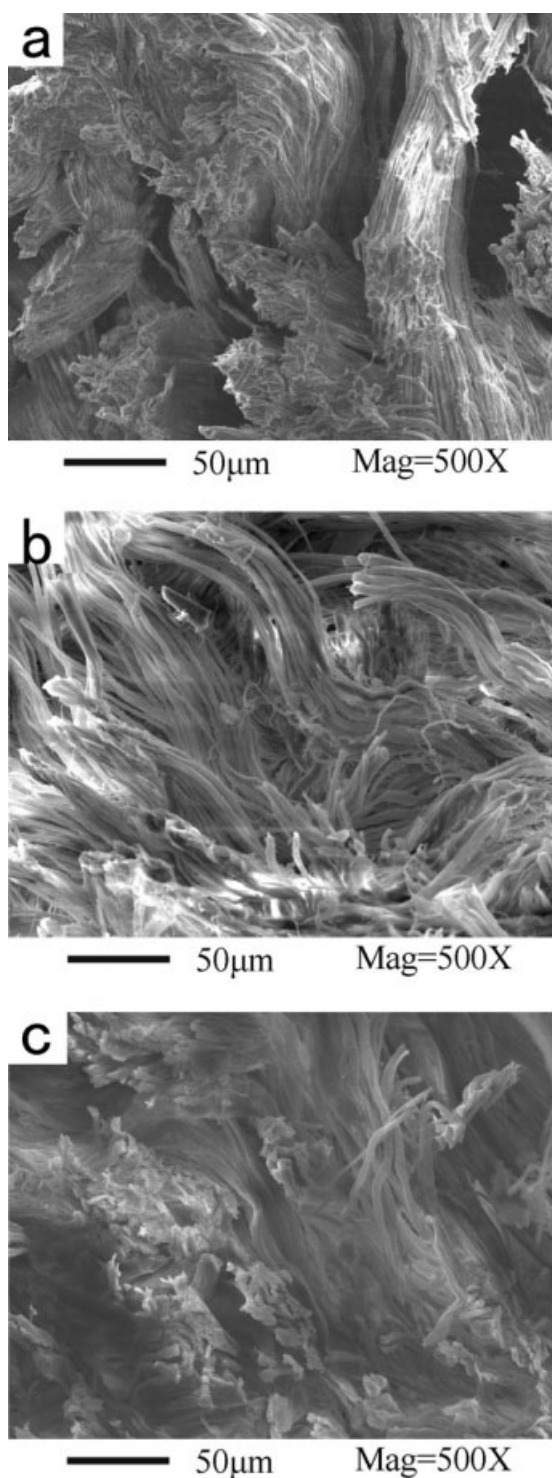


Figure 4 SEM images of the samples (side surface) treated at 38°C and 12 MPa under different time (a) 60 min, (b) 180 min, and (c) 300 min.

increase of temperature will induce the decrease of density of CO₂ and the amount of CO₂ absorbed by the samples, which is a negative factor. Therefore, at some intermediate temperature, the equilibrium of above factors can be achieved and the optimal looseness result can be observed.

BET surface area of samples

Nitrogen adsorption/desorption study is an effective method to investigate the changes of surface area. Figure 8 shows the N₂ adsorption–desorption isotherms of original and treated samples. Type III isotherms were obtained for these samples, according

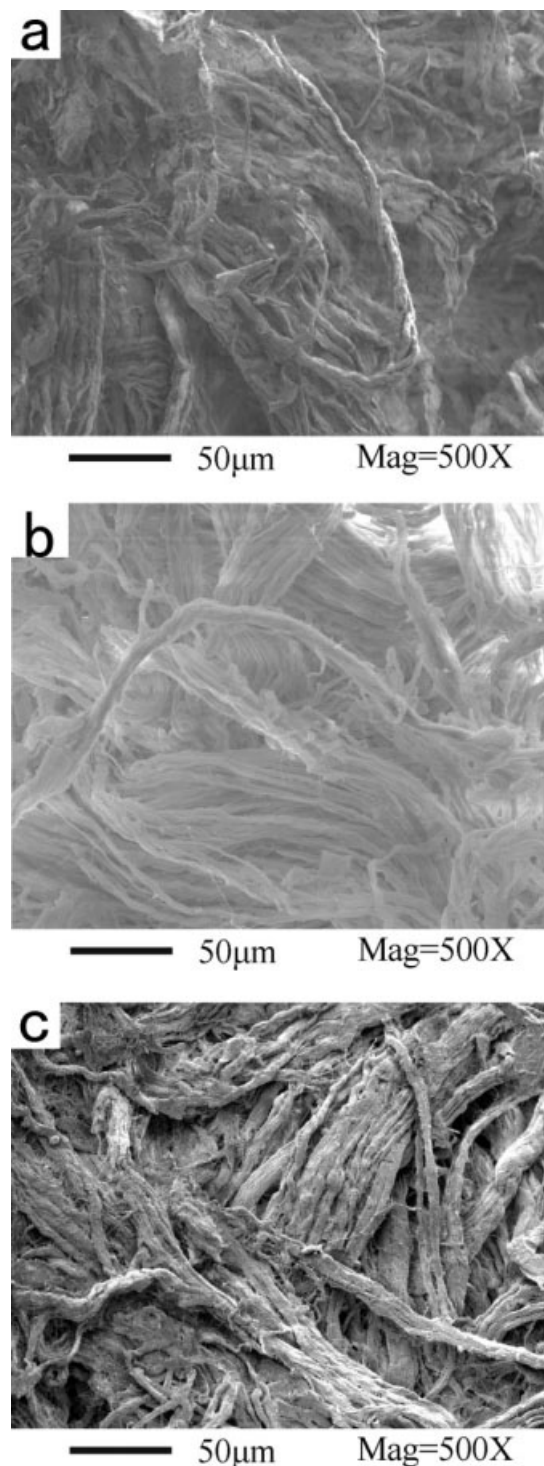


Figure 5 SEM images of the samples (inner surface) treated at 38°C and 12 MPa under different time (a) 60 min, (b) 180 min, and (c) 300 min.

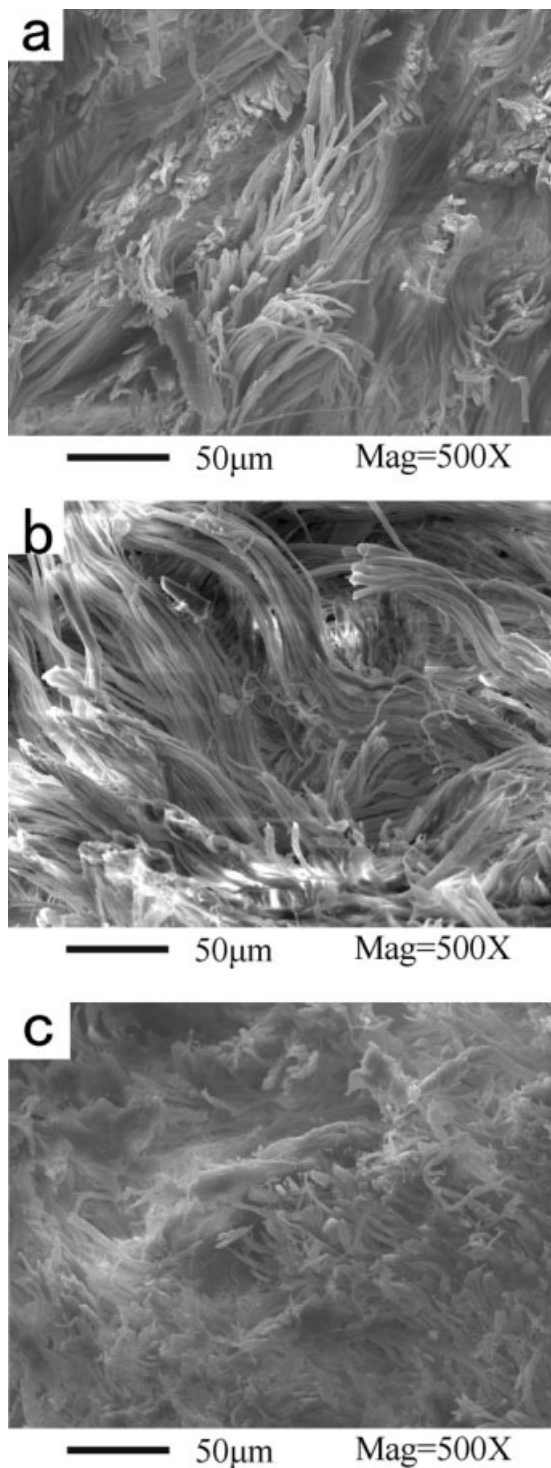


Figure 6 SEM images of the samples (side surface) treated at 12 MPa for 180 min under different temperatures (a) 33°C, (b) 38°C, and (c) 43°C.

to the IUPAC nomenclature. Pore size distribution of samples calculated by the BJH method from nitrogen desorption isotherms are as shown in the inset of Figure 8. It is found that if the pore size distribution of treated sample changes a little, however, the BET

surface area of the samples increases from 1.67 m²/g to 6.33 m²/g after treated by supercritical CO₂.

Table I shows the detailed data of the BET surface area of the samples prepared under different experimental conditions. Samples 2–4 were prepared in

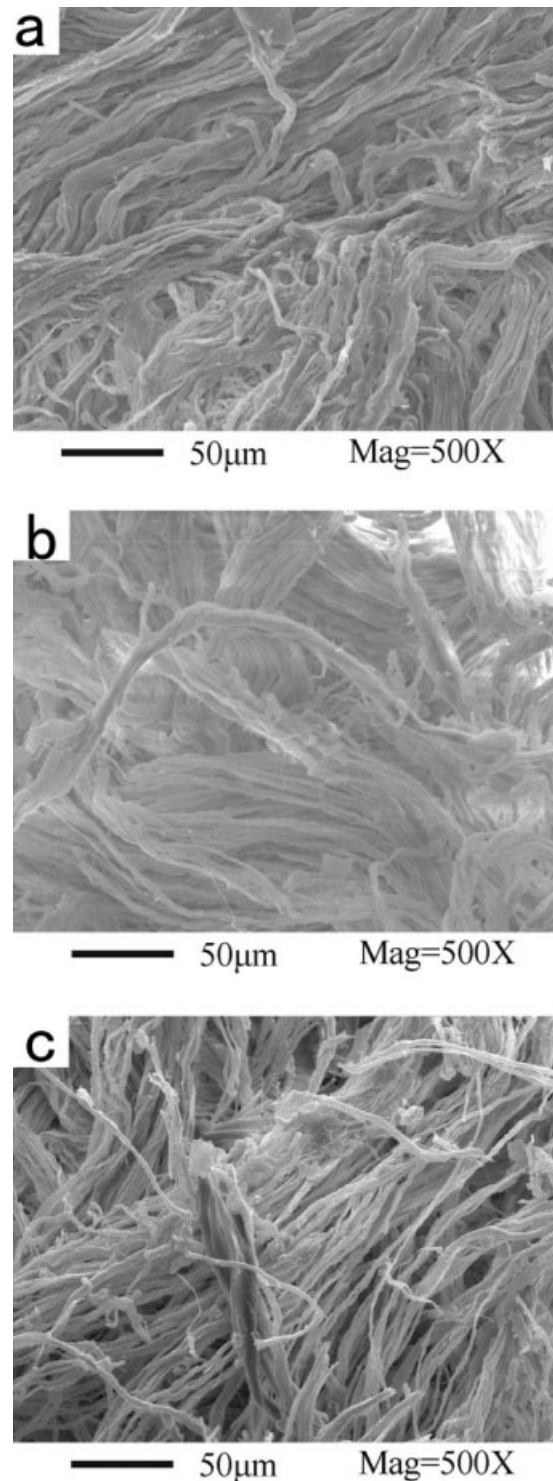


Figure 7 SEM images of the samples (inner surface) treated at 12 MPa for 180 min under different temperatures (a) 33°C (b) 38°C, and (c) 43°C.

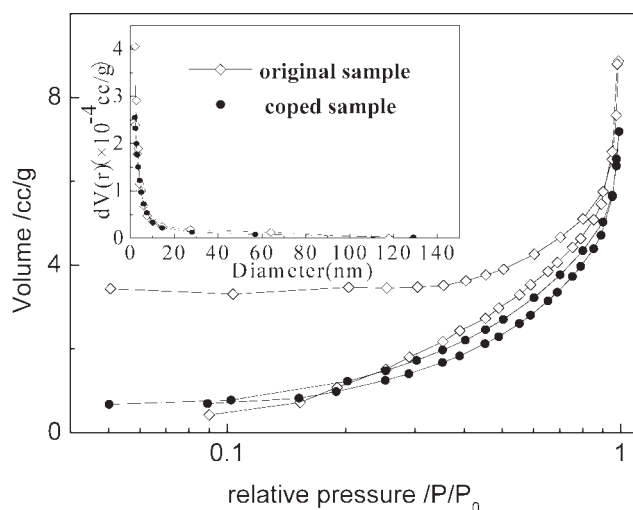


Figure 8 N₂ adsorption–desorption isotherms and BJH pore radius of original sample, and treated one prepared at 12 MPa, 38°C in SC-CO₂ for 180 min.

SC-CO₂ at 38°C and at the pressure range from 8 to 16 MPa. It can be seen that the BET surface area of the products all increase compared with that of the untreated sample, and maximum of 6.33 m²/g was obtained at 12 MPa. Similarly, among these Samples 3, 5–6, which were all prepared in SC-CO₂ at 12 MPa and 38°C in the time range from 60 to 300 min, the BET surface area of the samples treated at 180 min were the maximum. However, comparing Samples 3, 7, and 8, we will find that the BET surface area of the products increase with the temperature and can come up to 7.53 m²/g at 43°C, the mechanism of temperature's effect on BET surface area of samples needs to be further studied.

XRD analysis

To investigate the effect of the supercritical CO₂ on the structure, XRD patterns were introduced to study the changing of aggregation structure in selected samples (Fig. 9). There are three apparent

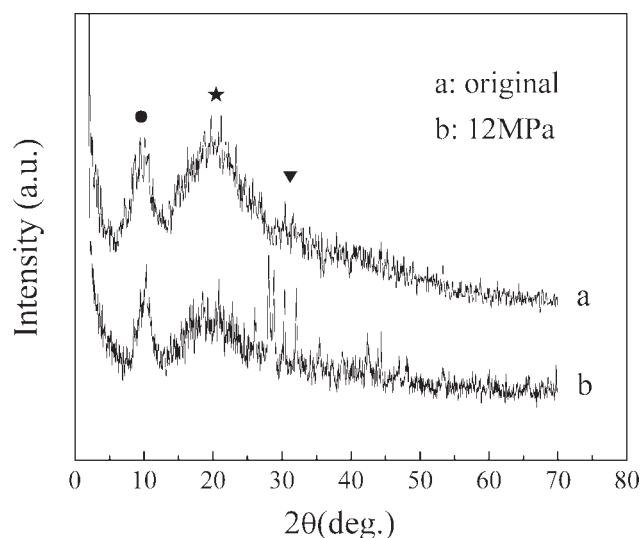


Figure 9 X-ray diffraction patterns of (a) original sheepskin piece sample; (b) samples treated at 12 MPa, 38°C, 180 min.

peaks in X-ray diffraction patterns of collagen. According to the literature,²⁴ the first sharp peak at 9.5° indicates the distance between the molecular chains, the broad peak at 20.4° is due to diffuse scattering and the third peak at 30.4° corresponding to the unit height, typical of the triple helical structure. It can be observed that, referring the sample treated at 12 MPa, 38°C for 180 min, the first intense peak was sharper, indicating that the decreasing of interplanar spacing led to the degree of order increasing in ordered regions. At the same time, the intensity of broad peak decreased compared with the original sheepskin, and it demonstrates that the multifarious arrangement structures in amorphous regions were loosened after treated at this condition. That is, compared with the original sample, the treated sample was loosened visibly, and the loosening of leather mostly happened in amorphous regions. It is noted surprisingly that there are three new sharp peaks appear close to 30°, they indicate the treatment of SC-CO₂ has apparent effect on the triple helical structure in the collagen fiber.

TABLE I
BET Surface Area of Samples Prepared Under Different Conditions

Sample	Pressure (MPa)	Time of constant pressure (min)	Temperature (°C)	BET surface area (m ² /g)
1		Original sample		1.67
2	8	180	38	3.64
3	12	180	38	6.33
4	16	180	38	2.71
5	12	60	38	2.12
6	12	300	38	1.68
7	12	180	33	3.61
8	12	180	43	7.53

Tensile characteristics of the sample

To study the tensile properties of products, tensile strength, and elongation at break were characterized by a tensile analyzing test at temperature 20°C ± 2°C and humidity 65% ± 2%. Table II shows the detailed data of tensile strength and elongation of different samples treated at different experimental conditions. From this table, it can be seen that the elongation at break of the treated samples can increase to 128.2% compared with 95.9% of the original ones; however, the tensile strength of samples 2–3 decreases a little. Usually for the natural leather,

TABLE II
Tensile Strength and Elongation at Break of Samples
Prepared Under Different Conditions

Sample	Treated Condition	Tensile strength (MPa)	Elongation at break (%)
1	Untreated	14.7	95.9
2	10 MPa, 38°C, 3 h	13.9	117.6
3	12 MPa, 38°C, 3 h	11.7	128.2
4	14 MPa, 38°C, 3 h	16.3	124.7
5	12 MPa, 43°C, 3 h	16.2	119.3

the high tensile breaking strength owns to those physical and chemical interaction points, which are formed by hydrogen bonding or polar functional groups. When the samples were treated by SC-CO₂, the distance of collagen molecules would increase, and it is easier for these molecules to move. Therefore, the elongation increased yet the tensile strength decreases. Furthermore, it is interesting to find that both tensile strength and elongation at break increase considered of Samples 4–5. The mechanism is not clear and need to be further studied.

CONCLUSIONS

The loosening preparation of sheepskin fiber in supercritical CO₂ has been studied as a function of experimental pressure, temperature, and time. The loosened samples' morphology and tensile properties can be controlled by the process conditions and the results confirm the versatility of SC-CO₂ in loosening process. Moreover, the experimental parameters have different influence on samples. In the lower pressure range, the final looseness of the samples showed an inclination to increase with pressure, whereas looseness did not increase any more in the higher pressure range. Time and temperature are another decisive factor governing the structure of the product. SEM images and N₂ adsorption-desorp-

tion experiment have indicated that SC-CO₂ treatment on the fiber have apparent positive effect (such as making the fiber more loosened and order). Besides, after treated at any conditions by SC-CO₂, elongation at break of all the samples can increase.

References

- Nazer, D. W. *J Cleaner Prod* 2006, 14, 65.
- Hüffer, S.; Taeger, T. *J Am Leather Chem Assoc* 2004, 99, 423.
- Sivakumar, V.; Rao, P. G. *J Cleaner Prod* 2001, 9, 25.
- Sivakumar, V.; Rao, P. G. *Ultrason Sonochem* 2003, 10, 85.
- Peng, B. *Ultrason Sonochem* 2007, 14, 305.
- Mfintysalo, E.; Marjoniemi, M.; Kilpeläinen, M. *Ultrason Sonochem* 1997, 14, 141.
- Schramm, W. *J Cleaner Prod* 1997, 5, 291.
- Santos, L. M.; Gutterres, M. *J Cleaner Prod* 2007, 15, 12.
- Sreeram, K. J.; Ramasami, T. *Resour Conserv Recy* 2003, 38, 185.
- Marsal, A.; Celma, P. J.; Cot, J.; Cequier, M. *J Supercrit Fluids* 2000, 16, 217.
- Vaquero, E. M.; Beltrán, S.; Sanz, M. T. *J Supercrit Fluids* 2006, 37, 142.
- Cantero, R.; Canals, T.; Iturriaga, H. *Talanta* 2007, 71, 1690.
- Caries, M.; Perre, C.; Gavend, G. *IULTLS Congress; Friedrichshafen, 1955*, 37.
- Fischer, W.; Nickolaus, G. *Leder* 1990, 41, 174.
- Meyer, A.; Kleiböhmer, W. *J Chromatogr A* 1995, 718, 131.
- Ahlström, L. H.; Björklund, E.; Mathiasson, L. *Anal Bioanal Chem* 2005, 382, 1320.
- Ahlström, L. H.; Sabine, A.; Mathiasson, L. *J Sep Sci* 2005, 17, 2047.
- Eskilsson, C. S.; Davidsson, R.; Mathiasson, L. *J Chromatogr A* 2002, 955, 215.
- Garrigós, M. C.; Reche, F.; Marín, M. L.; Jiménez, A. *J Chromatogr A* 2002, 976, 309.
- Glenon, J. D.; O'Connell, M.; Leahy, S. *99-Global Symposium on Recycling, Waste Treatment and Clean Technology Proceedings; San, Sebastian, Spain, 1999*; 2329.
- Minamiura, M.; Moriyoshi, T.; Katoh, S.; Nakanishi, T. *EP Pat.* 1505162 (2005).
- Geihlsler, H.; Weidner, E. *U.S. Pat.* 5,900,027 (1999).
- Pechdo, C. *International Cleaner Technology Seminar; Birmingham, 1995*; 60.
- Giraud-Guille, M. M.; Besseau, U.; Chopin, C. *Biomaterials* 2000, 21, 899.