Behavior of Fatliquored Leathers in a Microwave Field

by

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Abstract

Leathers fatliquored with sulfited fish oil were irradiated with microwave at various intensities, then their physical properties and the microstructure of collagen fibers were investigated to show the roles of microwave field. As confirmed, the free and capillary moisture in leather were firstly removed by microwave radiation, accompanying with diminution in area. However, the hydrothermal stability of leather was scarcely altered. Scanning Electron Microscope images indicated that the dispersion of collagen fibers was not destroyed with microwave exposure. In addition, the characteristic D-periodicity and microstructure for the collagen were changed little as revealed by Atomic Force Microscope and X-ray Diffraction studies. Furthermore, there was some improvement in the softness of leathers because of migration of oil and its uniform distribution. These results could be helpful for understanding the roles of microwave technique in leather industry.

Resumen

Cueros engrasados con aceite de pescado sulfitado fueron irradiados con [energía] de micro-ondas a varias intensidades, y luego sus propiedades físicas, así como la microestructura de las fibras del colágeno fueron investigadas para demostrar los efectos de los campos electromagnéticos de microondas. Tal como confirmado, la humedad libre así como la capilar, fueron las aguas inicialmente removidas por la radiación de microondas con una consecuente disminución del área. Sin embargo, la estabilidad hidrotérmica del cuero escasamente se alteró. Las imágenes por medio de microscopía electrónica por barrido indicaron que la dispersión de las fibras colagénicas no se destruyó por la exposición a la radiación por microondas. Adicionalmente la característica periocidad-D y la microestructura del colágeno, no cambiaron significativamente tal y cual se observó por Microscopía de Fuerza Atómica y estudios de Difracción de Rayos-X. Más aun, hubo mejoría en la blandura de los cueros por la migración del engrase y en su uniforme distribución. Estos resultados podrían ser útiles en la comprensión de las aplicaciones de la técnica de microondas en la industria del cuero.

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Manuscript received June 25, 2011, accepted for publication October 29,2011

INTRODUCTION

Microwave, an electromagnetic wave with frequency between 300 MHz and 300 GHz, is extensively used in industries (such as, the food and medicine field[1]) to shorten reaction time and save energy.[2] Analogously, there are several attempts on using microwave technique in leather manufacture, including tanning,[3] dyeing[4,5] and drying.[6-13] As reported, the color rub fastness could be enhanced markedly if dyed leathers were further exposed to a moderate microwave field, also, 20% energy would be saved by microwave irradiation as compared with the conventional hot air drying. As shown by Komanowsky M. study, unhaired, delimed and wrung hides were still relatively soft and flexible if they were dried to the moisture content (between 33% and 38% on dry basis) in slowly rotating mixers or specially adapted tanning machines (such as drums or hide processors) with microwave under vacuum. The previously reported studies revealed many advantages with microwave exposure. However, they did not mention the changes of the chemicals in leathers and the microstructure of collagen fibers in a microwave field, the scarce understanding of which probably prevent the adoption of microwave in leather industry.

During leather manufacture, fatliquoring is an important process to impart leathers softness by means of oil distributed inside and outside the collagen fibers,[14,15] and its distribution uniformity may be greatly altered with some "heat flow" in the following drying process. In the present study, leathers treated with sulfited fish oil, were irradiated with microwave at various intensities, and then some physical properties of the leathers were tested, including softness and shrinkage temperature. In addition, the microstructure and morphology of collagen fibers and the oil distribution were investigated with Scanning Electron Microscope, Atomic Force Microscope and X-ray Diffractometer. This study revealed the changes of the physical chemical properties of both fatliquored leather and the fatliquors. The results demonstrated that the distribution uniformity of the fatliquors in leather was improved in the end of microwave radiation, which was speculated as a reason to the increase in softness of the fatliquored leather.

EXPERIMENTAL

Materials

Bovine wet blues, with thickness about 2.4 mm, were sampled from a local tannery, and then prepared with an individual sulfited fish oil (*Derminol OS 1 liquid*, *OS*) using a typical bovine shoe upper fatliquoring procedure (see Appendix). *OS*, with oil content about 70%, was a commercial fatliquor from Clariant Chemical Corporation. Its dosage was 6% based on the weight of leather, and was almost exhausted during this fatliquoring trial.

Experimental set-up

The schematic diagram of an improved MCR-3S microwave set-up (Xi'an Yuhui Instrumental Co., China) is displayed in Fig. 1. This set-up has a capacity of 19.69 L (293 mm × 320 mm × 210 mm) and could provide microwave at 2450 MHz with the highest power as 800 W. The leather was proposed to be placed on an autorotation object stage, about 10 cm below the microwave source.

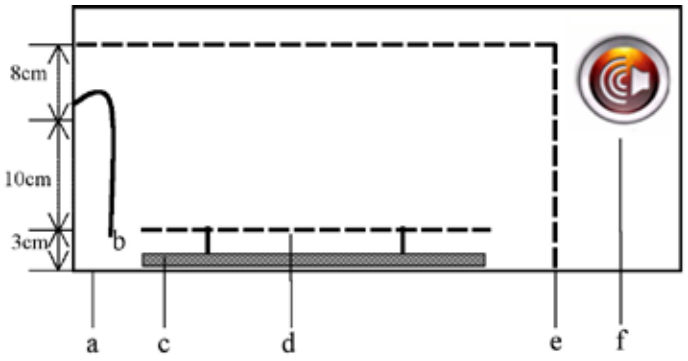

Figure. 1 Schematic diagram of the microwave set-up
a – microwave set-up, b – temperature sensor, c –autorotation object stage, d – plastic mesh grid, e – inside covering, f – microwave source

Microwave irradiation trials

Matched pieces (10 cm × 15 cm, about 40 gram) were taken from the back area of the fatliquored leather, and then prepared by wringing using a pair of steel cylindrical extrusion rolls (Φ5.5 cm×18 cm) with a pressure of 8 kg/cm^2, which lowered moisture content to a level of 65%. Next, the wrung leather pieces were sealed in a plastic bag for more than 24 h to balance their moisture content. Finally, these leather pieces were exposed to a microwave field (shown in Fig. 1) for 60 s with microwave power as 0, 80 W, 160 W, 240 W and 320 W, which corresponds to microwave intensities as 0, 4.06 W/L, 8.13 W/L, 12.19 W/L and 16.25W/L respectively.

Analyses of physical properties of leathers

Measurement of temperature on leather grain

The temperature on leather grain was measured with a FY-280 infrared thermometer (Shenzheng Futai Science and Technology Co., China) immediately after microwave exposure. Twelve uniformly distributed points were analyzed and the data were averaged to represent the temperature on leather grain.

Determination of face area yield (%)

The face area of leather was measured before and after microwave irradiation and the results were noted as S_0 and S_1 respectively. Then, the face area yield (%) was calculated as the following equation:

$$\text{Face area yield}(\%) = \frac{S_1}{S_0} \times 100\% \quad (1)$$

Three samples were tested and the data were averaged to represent the face area yield with microwave exposure.

Measurement of moisture content (%)
Moisture content in leather was determined as QB/T 3812.12-1999 method [16]. Three samples were analyzed and the data were averaged to represent the moisture content with microwave exposure.

Determination of shrinkage temperature
The shrinkage temperature of leather was measured as QB/T 2713-2005 method[17] using a MSW-YD4 shrinkage thermometer (Electron Institute of Shanxi Science and Technology University, China). Three samples, parallel to the back bone of leather, were determined and the data were averaged to represent the shrinkage temperature with microwave exposure.

Measurement of softness
The softness of leather was estimated according to ISO 17235-2002 method[18] using a GT-303 softness tester (Gotech Instrumental Co., China). Three samples were analyzed and the data were averaged to represent the softness with microwave exposure.

Characterization of collagen fibers in leathers
Scanning electron microscope study
A JSM-5900LV scanning electron microscope (Japan) was used for the analysis. The micrographs for the cross sections of leathers were obtained by operating the SEM at low vacuum (10^{-4} Pa) with an accelerating voltage of 20 kV in different magnification levels.

Atomic force microscope study
A SPM-9600 atomic force microscope (Japan) was exploited to observe the microstructure of the collagen fibers in leathers. The AFM images were obtained in ambient conditions at room temperature (20°C) with 65% relative humidity. The other testing conditions were as following: NSG 11 probe with observing size as 0.25 μm.

X-ray diffractometer study
An X'Pert Pro X-ray diffractometer (Netherlands) was used to obtain the X-ray diagrams for the grain surface of leathers. The testing conditions were as following: generator voltage as 40kV, tube current as 35 mA, 2θ as 5° to 60°, step size as 0.03°, time per step as 0.2 s.

Characterization of fatliquors
Dielectric constant study
The fatliquor *OS* was firstly dissolved in deionized water to get a 1% (mass content) solution. Then this solution was irradiated with microwave at an intensity of 16.25 W/L, and its temperature was raised up to 30°C, 40°C, 50°C and 60°C respectively. Next, the temperature was maintained for 10 min by discontinuous microwave radiation, which was automatically controlled by the microwave set-up (Fig. 1). The solutions, heated with water bath of equal temperature for 10 min, were as controls. The dielectric constants for the above solutions were determined with a DZJC dielectric constant tester (Nanjing Dazhan Institute, China) at the same temperature as the preparation process. Three measurements were carried out and the data were averaged to represent the dielectric constants.

Viscosity study
A liquor of 100 mL fatliquor was exposed to microwave at an intensity of 16.25 W/L, which elevated the temperature to 30°C, 40°C, 50°C and 60°C respectively. Then the temperature was maintained for 10 min by discontinuous microwave radiation, which was automatically controlled by the microwave set-up (Fig. 1). The solutions, heated with water bath of equal temperature for 10 min, were as controls. The viscosity of the fatliquor was analyzed with a SNB-1 numerical viscosity tester (Nirun Intellectual Scientific Corporation, China) at the same temperature as the preparation process. Three measurements were carried out and the data were averaged to represent the viscosity.

Determination of particle size in fatliquor solutions
The fatliquor *OS* was firstly dissolved in deionized water to get a 0.5% (mass content) solution. Then the solution was irradiated with microwave at an intensity of 16.25 W/L, and its temperature was raised up to 30°C, 40°C, 50°C and 60°C respectively. Next, the temperature was maintained for 10 min by discontinuous microwave radiation, which was automatically controlled by the microwave set-up (Fig. 1). The solutions, heated in water bath of equal temperature for 10 min, were as controls. The average size for the particles in fatliquor solutions was measured with a Nano ZS zetasizer (Malvern Corporation, England) at the same temperature as the preparation process. Three measurements were carried out and the data were averaged to represent the particle average size.

RESULTS AND DISCUSSION

Physical properties
Several changes were found for the leathers after they were exposed to a microwave field. For example, as shown in Tab. 1, the moisture content fell accompanying with the rise of the temperature of leather. When the microwave intensity was increased to 16.25 W/L, the moisture content decreased from the initial 64.7% to 58.3%, and the grain temperature rose to 64.8°C. Furthermore, uniform temperature and moisture distribution were found throughout the leather with microwave exposure, which was similar to Komanowsky study.[12,13]

TABLE 1
Moisture content and grain temperature of leathers with microwave exposure

Microwave intensity (W/L)	Moisture content (%)	Temperature (°C)
0	64.7 ± 0.3	23.9 ± 0
4.06	63.5 ± 0.2	39.3 ± 0.9
8.13	62.4 ± 0.4	51.2 ± 1.2
12.19	61.1 ± 0.4	57.9 ± 1.2
16.25	58.3 ± 0.4	64.8 ± 1.2

Three experienced tanners were invited for visual assessment for grain smoothness, softness, depth of shade and general appearance. These organoleptic properties were rated on a scale of 1-10 with 1 as the lowest and 10 as the best. The average of ratings has been calculated for each property and taken for comparison. As demonstrated by Tab. 2, there was scarce change in the organoleptic properties of the leathers with microwave exposure.

The face area of leather was minified(sic) when the microwave intensity was higher than 8.13W/L (face area yield data not shown). As we know, moisture in leather was identified as three types: free water, capillary water and combined water. Thereinto(sic), the leather would shrink distinctively if the combined water was removed. The diminishing in area was only about 3% even if the microwave intensity was elevated to 16.25W/L. These results indicated that most of the water removed by microwave heating was free moisture and capillary moisture, which would not distinctly affect the organoleptic properties of leather (shown in Tab. 2). The shrinkage temperature was shown in Fig. 2(a). The shrinkage temperature only varied within the range of 2°C after the leather was exposed to a microwave field, which proved that microwave irradiation would not influence the thermostability of leathers.

As displayed in Fig. 2(b), the softness of leather rose with microwave intensity. When the microwave intensity was raised to 16.25 W/L, the softness increased sharply from the initial 5.15 mm to 5.75 mm.

SEM analyses

The scanning electron micrographs for the cross-sections of leathers were shown in Fig. 3. The images with different magnifications revealed the collagen fibers in the papillary and reticular layers of leathers. There was slight variation in both the morphology and dispersion of the collagen fibers

TABLE 2
Visual assessment data of organoleptic properties of leathers

Microwave intensity(W/L)	Grain smoothness	Softness	Depth of shade	General appearance
0	8.0 ± 0.25	8.0 ± 0.25	7.0 ± 0.25	7.7 ± 0.25
4.06	8.0 ± 0.25	8.0 ± 0.25	7.0 ± 0.25	7.7 ± 0.25
8.13	8.0 ± 0.25	8.0 ± 0.25	7.0 ± 0.25	7.7 ± 0.25
12.19	7.5 ± 0.25	8.5 ± 0.25	7.0 ± 0.25	7.7 ± 0.25
16.25	7.5 ± 0.25	8.5 ± 0.25	7.0 ± 0.25	7.7 ± 0.25

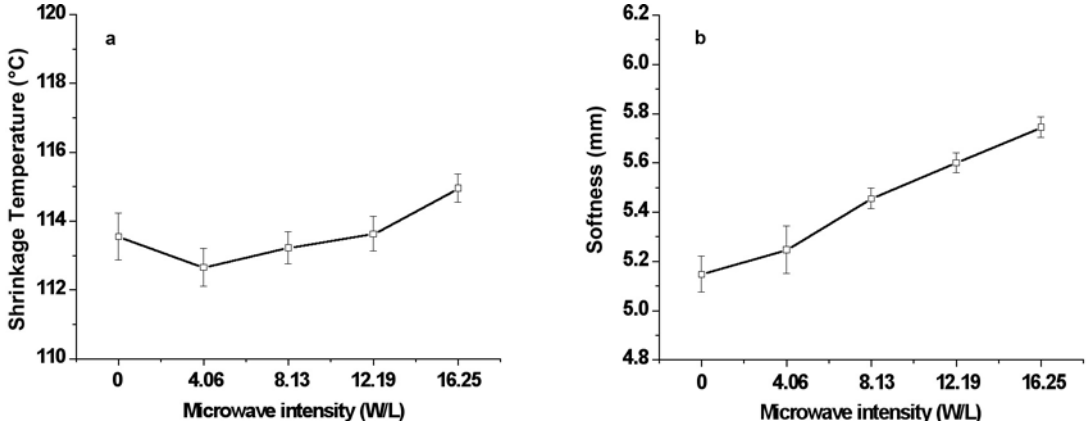

Figure 2. Shrinkage temperature (a) and softness (b) for leathers.

after the leather was exposed to a microwave field, which confirmed that moderate microwave irradiation would not destroy the microstructure and porosity of fatliquored leathers.

AFM analyses

The microstructure for the collagen fibers was demonstrated in Fig. 4. The collagen fibers were characteristic axial *D*-periodic cross-striated fibrils; where *D* was between 35 nm and 40nm, lower than the *D*-periodicity (*about 67nm*) of the native collagen in raw hide.[19-21]These results further proved that the microstructure of collagen was not affected with microwave exposure. The surface of collagen fiber was not smooth as displayed by the AFM images (Fig. 4), and there was some stacking of leather chemicals, most of which were speculated as oil according to the properties of the chemicals used for the preparation of fatliquored leathers. Fig. 4 also demonstrated that the stacked oil became to distribute uniformly by microwave exposure.

XRD analyses

Fig. 5 showed the X-ray diagrams for fatliquored leathers after they were exposed to a microwave field. There were two peaks in all X-ray curves, the diffraction angle (2θ) of which were located at about 7.0° and 21.2°. As reported, the two peaks in the X-ray diagram of the collagen fiber in the hide/leather represented the side-chain distance peak (Peak 1) and the backbone reflection peak (Peak 2).[22-24] In this study, the existence of the two peaks further confirmed that the microstructure of collagen fibers was not deteriorated with microwave radiation. The decrease in the intensity of the two peaks may be due to the migration and uniform distribution of oil as revealed by AFM analyses.

Properties of fatliquors

The dielectric constants (ε) for fatliquors were indicated in Fig. 6. The ε values were higher than a level of 10^3, either the fatliquors were heated with water bath or with microwave irradiation. It was speculated that the counter ions in the double-layer of the fatliquor colloidal particles migrated resulting in a surface capacitance and a magnified 'apparent' dielectric constant. These findings were analogous to the dielectric constants for the suspensions of colloidal particles in aqueous electrolyte solutions reported by Marshall Fixman.[25]

Also, Fig. 6 demonstrated that the dielectric constants were higher for the fatliquors exposed to a microwave field. Microwave radiation would induce the dipole relaxation of the water molecules and further accelerate the migration of the counter ions in double layers of colloidal particles leading to the increase of the apparent dielectric constants. As displayed in Fig. 7(a), the viscosity for the fatliquors fell with the rising temperature. Moreover, the viscosity decreased sharply by microwave irradiation, and it dropped to a level of lower than 10mPa.s (data not shown). Similarly, the average size for the fatliquor particles decreased with the temperature, and it fell rapidly with microwave exposure (Fig. 7(b)). As we know, both the viscosity and the average size for the fatliquor particles would affect the penetrability and filling ability of fatliquors. The variations in fatliquor solutions caused by microwave irradiation were helpful for the flowing of oils, which could further promote the migration of leather chemicals (such as, oils, dyes) and improve their distribution uniformity.

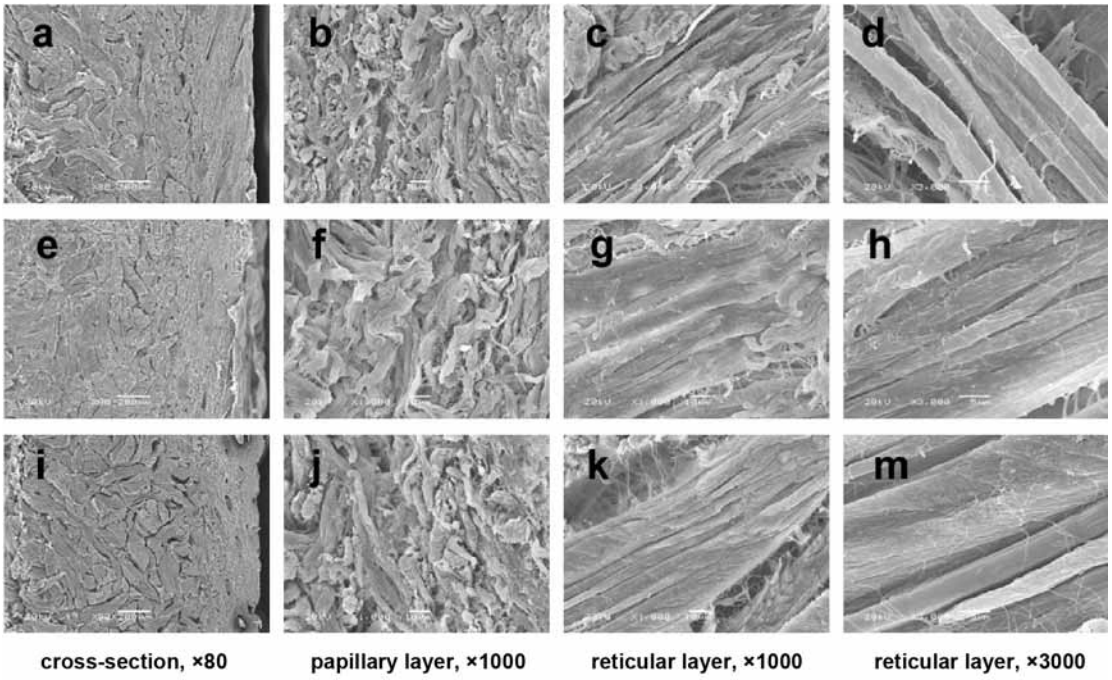

Figure 3. SEM images for the fatliquored leathers. (Microwave intensity: a, b, c, d as 0 W/L; e, f, g, h as 8.13 W/L; i, j, k, m as 16.25 W/L.)

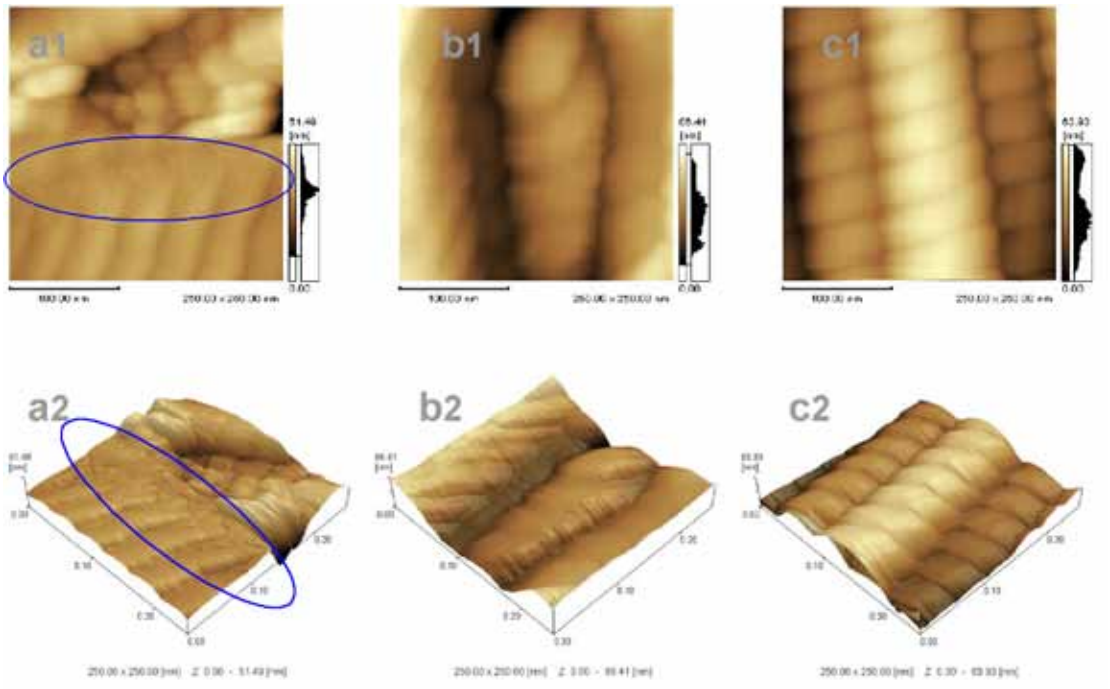

Figure 4. AFM images for fatliquored leathers. (Microwave intensity: a1, a2 as 0 W/L; b1, b2 as 8.13 W/L; c1, c2 as 16.25 W/L.)

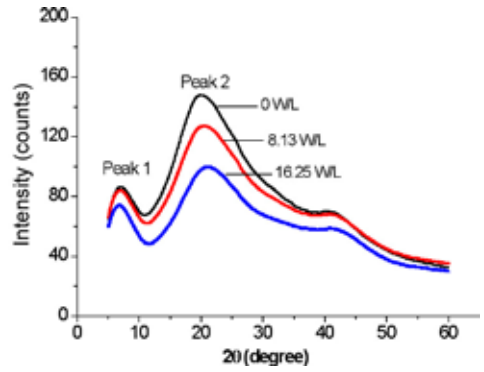

Figure 5. X-ray diagrams for fatliquored leathers

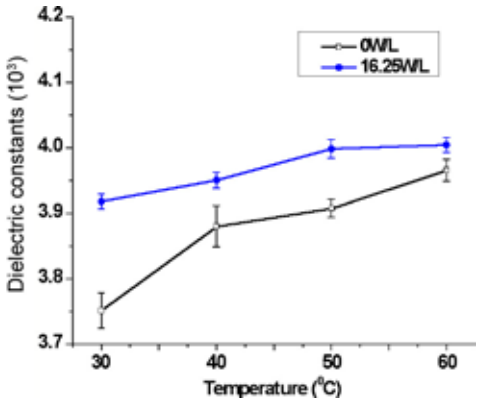

Figure 6. Dielectric constants for fatliquor solutions. (Mass content as 1%; '0 W/L' represented heating with water bath; '16.25 W/L' represented preparing with microwave irradiation.)

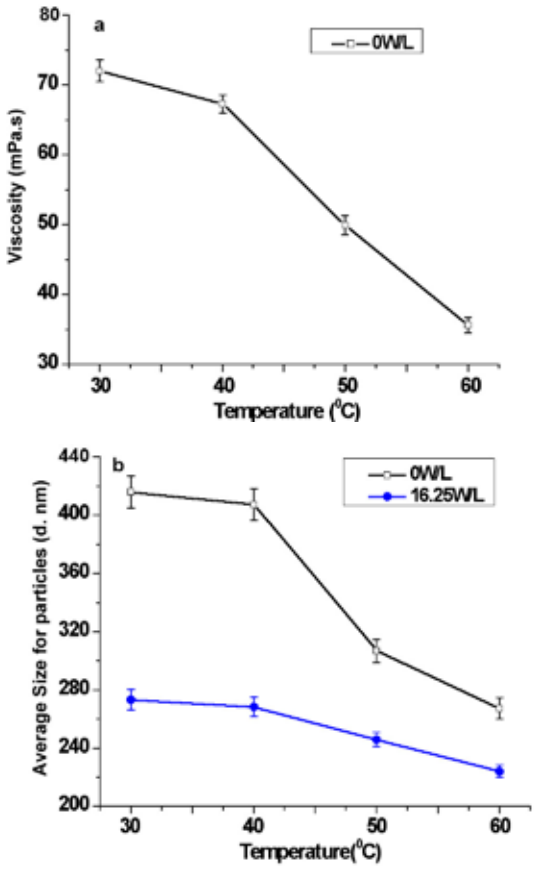

Figure 7. Physical chemical properties of fatliquors. ('0 W/L' represented heating with water bath. '16.25 W/L' represented preparing with microwave irradiation. (a) viscosity of the original fatliquors; (b) average size for the particles in 0.5% (mass content) fatliquor solution.)

DISCUSSIONS

The temperature of leather increased after microwave radiation, and the microwave energy caused evaporation of moisture inside the leather "from the inside out", permitting it to retain its porosity, both of which were analogous to Komanowsky study.[12,13] The viscosity and the average size of particles for the fatliquors decreased sharply in the end of microwave exposure, accompanying with the increase in their dielectric constants, which would further strengthen their response to microwave and promote their flowing through the pores in leather. As a result, more uniform distribution of fatliquors was found in the leather with microwave exposure. This was speculated as a reason to the rise in the softness of the fatliquored leather with microwave. What is more, the retained porosity during microwave radiation would be helpful for the migration of other chemicals like dyestuffs, resulting in evident improvement in their distribution uniformity. This view could be utilized to illustrate the homogeneous dye distribution in the leather colored with microwave radiation.[4,5]

CONCLUSIONS

Several techniques were exploited to characterize the variations in the fatliquored leathers and the fatliquors with moderate microwave exposure. The porosity in leather and the microstructure for both collagen and collagen fibers are retained during the microwave radiation. The fatliquors were prone to flow because of the decrease in both the viscosity and the average size for their colloidal particles in the microwave field, which led to homogeneous oil distribution in leather and enhancement in the softness of the fatliquored leathers. It is expected that microwave could be exploited to improve the distribution uniformity of leather chemicals.

ACKNOWLEDGEMENT

The authors wish to thank the Ministry of Science and Technology of China for the financial support (Item No. 2006DFA41010, Item No. 2009DFA42850).

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APPENDIX

Bovine wet blues were neutralized, retanned and fatliquored to obtain fatliquored leathers. The detailed procedures were shown in Tab. 3.

TABLE 3
Fatliquoring process of bovine leather

Procedures	Chemicals	Dosage (%)	Temperature (^{0}C)	Time (min)	pH requirement
Rewetting	water	300	30	60	
Neutralization	Water	100	40		
	Sodium formate	1		60	
Retanning	Chrome tanning agent *HLS-A powder*	3		60	
	Sodium bicarbonate	1		40	6.0 - 6.5
Fatliquoring	**Fatliquoring agent** *Derminol OS 1 liquid*	6	60	120	5.5 - 6.0
	Sodium formate	2		60	3.0 - 3.5
Washing	water	300	40	10	