Paper C6

Behaviors of fat liquored leathers in a microwave field

Gong Ying [1,2], Zhang Tao [1], Chen Wuyong [1,*]

[1] National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, Sichuan, China, Email address: wuyong.chen@163.com

[2] Chongqing Academy of Metrology and Quality Inspection, 401123, Chongqing, China.

Abstract

Leathers fat liquored with sulfited fish oil were irradiated with microwave at various intensities and then their physical properties and the microstructure of collagen fibers were investigated to show the influences of microwave field. As confirmed, the free and capillary moisture in leather were firstly removed by microwave radiation, accompanying with diminution in area. However, there was little change in the hydrothermal stability of leathers. Microstructure analysis results indicated that the dispersion of collagen fibers and their characteristic D-periodicity and crystallinity for the collagen were not destroyed. While there was some improve in the softness of leathers because of distinct migration of oil and its uniform distribution. These results could be helpful for understanding the roles of microwave technique in leather industry.

Keywords: microwave, leather, collagen fibers, microstructure, softness, fat liquors

1. Introduction

Microwave, an electromagnetic wave with frequency between 300MHz and 300GHz, 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 [4-6] and drying [7-11]. 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. Although microwave radiation brings about such improvements, it is not commonly used in leather industry except assisting drying. Obviously, it is necessary to understand the influences of microwave radiation on the properties of leathers in order to promote the use of microwave technique.

As we know, fatliquoring is an important process to impart leathers softness by means of oil distributed inside and outside the collagen fibers [12,13], the distribution uniformity of which may greatly alter with some “heat flow” in the following drying process. In the present study, leathers, previously prepared 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.

2. Experimental

2.1 Materials

Bovine wet blues, with thickness about 2.4mm, 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. *OS*, with oil content about 70%, was commercial fat liquor from Clariant Chemical Corporation. Its dosage was 6% based on the weight of leather, and was almost exhausted during this fatliquoring trial.

2.2 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 19.69L (293mm × 320mm × 210mm) and could provide microwave at 2450MHz with the highest power as 800W. The leather is proposed to be placed on an autorotation object stage, about 10cm below the microwave source.

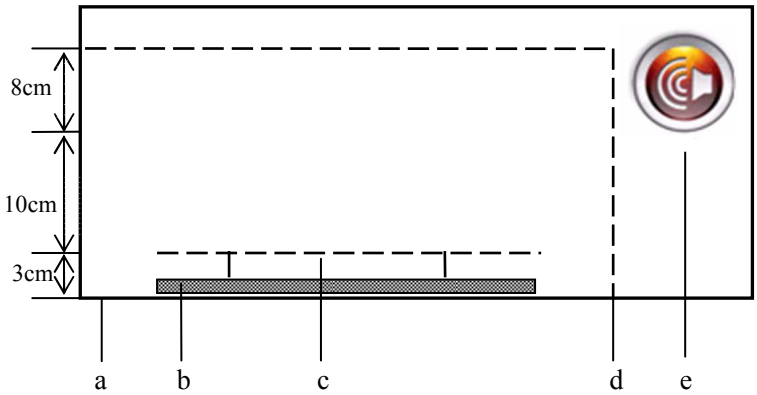


Fig. 1 Schematic diagram of the microwave set-up

a – microwave set-up, b – autorotation object stage, c – plastic mesh grid, d – inside covering, e – microwave source

2.3 Microwave irradiation trials

Matched pieces (10cm × 15cm) were taken from the back area of the fat liquored leather, and then prepared by wringing with a pressure of 8kg/cm^2, which lowered moisture content to a level of 65%. Next, the wringed leather pieces were sealed in a plastic bag for more than 24 hr to balance their moisture content. Finally, these leather pieces were exposed to a microwave field (as shown in Fig. 1) for 60s with microwave power as 0, 80W, 160W, 240W and 320W, which corresponds to microwave intensities as 0, 4.06W/L, 8.13W/L, 12.19W/L and 16.25W/L separately.

2.4 Analyses of physical properties of leathers

2.4.1 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) shortly after microwave exposure.

Twelve uniformly distributed points were analyzed and the data were averaged to represent the temperature on leather grain.

2.4.2 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:

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

2.4.3 Measurement of moisture content (%)

Moisture content in leather was determined as QB/T 3812.12-1999 method [13].

2.4.4 Determination of shrinkage temperature

The shrinkage temperature of leather was measured as QB/T 2713-2005 method [14] using a MSW-YD4 shrinkage thermometer (Electron Institute of Shanxi Science and Technology University, China).

2.4.5 Measurement of softness

The softness of leather was estimated according to ISO 17235-2002 method [15] using a GT-303 softness tester (Gotech Instrumental Co., China).

2.5 Characterization of collagen fibers in leathers

2.5.1 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 20kV in different magnification levels.

2.5.2 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. The other testing conditions were as following: NSG 11 probe with observing size as 0.25μm.

2.5.3 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 35mA, 2θ as 5° to 60°, step size as 0.03^o, time per step as 0.2s.

2.6 Characterization of fat liquors

2.6.1 Dielectric constant study

The fat liquor *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 16.25W/L, and its temperature was raised up to 30□, 40□, 50□ and 60□ separately. Next, the temperature was maintained for 10min by continual microwave radiation. The solutions, heated with water bath of equal temperature for 10min, 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.

2.6.2 Viscosity study

A liquor of 100mL fat liquor was exposed to microwave at an intensity of 16.25W/L, which elevated the temperature to 30□, 40□, 50□ and 60□ separately. Then the temperature was maintained for 10min by continual microwave radiation. The solutions, heated with water bath of equal temperature for 10min, were as controls.

The viscosity of the fat liquor was analyzed with a SNB-1 numerical viscosity tester (Nirun Intellectual Scientific Corporation, China) at the same temperature as the preparation process.

2.6.3 Determination of particle size in fat liquor solutions

The fat liquor *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 16.25W/L, and its temperature was raised up to 30□, 40□, 50□ and 60□ separately. Next, the temperature was maintained for 10min by continual microwave radiation. The solutions, heated in water bath of equal temperature for 10min, were as controls.

The average size for the particles in fat liquor solutions was measured with a Nano ZS zetasizer (Malvern Corporation, England) at the same temperature as the preparation process.

3. Results and discussion

3.1 Physical properties

Several variations were found for the leathers after they were exposed to a microwave field. For example, the moisture content fell accompanying with the rise of the temperature of leather. When the microwave intensity increased to 16.25W/L, the moisture content decreased from the initial 65% to 58%, and the grain temperature rose to 65□. These results suggested that there was ***heating effect*** caused by microwave radiation.

The face area minified when the microwave intensity was higher than 8.13W/L. As we know, moisture in leather was identified as three types: free water, capillary water and combined water. Thereinto, the face area 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. Meanwhile, there is scarce change in the organoleptic properties of the leathers. These results indicated that most of the water removed by microwave heating was free moisture and capillary moisture.

The shrinkage temperature (*Ts*) data were shown in Fig. 2(a). *Ts* just varied within the range of 2□ after the leather was exposed to a microwave field, which proved that microwave irradiation would not destroy the thermostability of leathers.

The softness for the leather was displayed in Fig. 2(b). The softness rose by microwave radiation. When the microwave intensity was raised to 16.25W/L, the softness increased

sharply from the initial 5.15mm to 5.75mm.

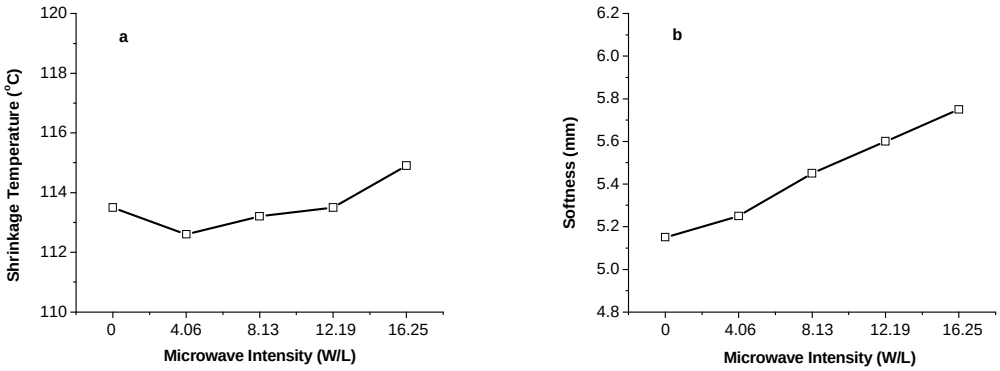
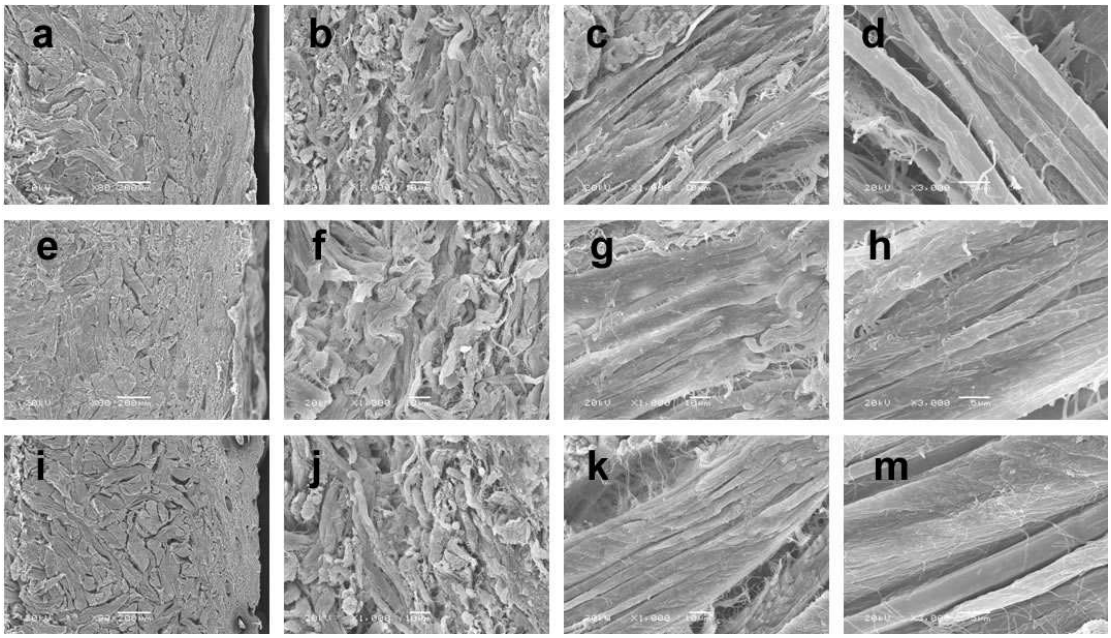


Fig. 2 Shrinkage temperature (a) and softness (b) for leathers

3.2 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 after the leather was exposed to a microwave field, which confirmed that moderate microwave irradiation would not destroy the microstructure of fat liquored leathers.



cross-section, ×80 papillary layer, ×1000 reticular layer, ×1000 reticular layer, ×3000

Fig. 3 SEM images for the fat liquored leathers

(Microwave intensity: a, b, c, d as 0 W/L; e, f, g, h as 8.13W/L; i, j, k, m as 16.25W/L.)

3.3 AFM analyses

The microstructure for the collagen fibers demonstrated in Fig. 4. The collagen fibers were characteristic axial *D*-periodic cross-striated fibrils, where *D* was between 35 nm and 40nm, much lower than the *D*-periodicity (*about 67nm*) of the native collagen in raw hide [16-18]. These results further proved that the microstructure of collagen was not damaged in a microwave field.

The surface of collagen fiber was not smooth as displayed in the AFM images (Fig. 4), and there is some stacking of leather chemicals, most of which was speculated as oil according to the properties of the chemicals used for the preparation of fat liquored leathers. Fig. 4 also demonstrated that the stacked oil became to distribute uniformly by microwave exposure.

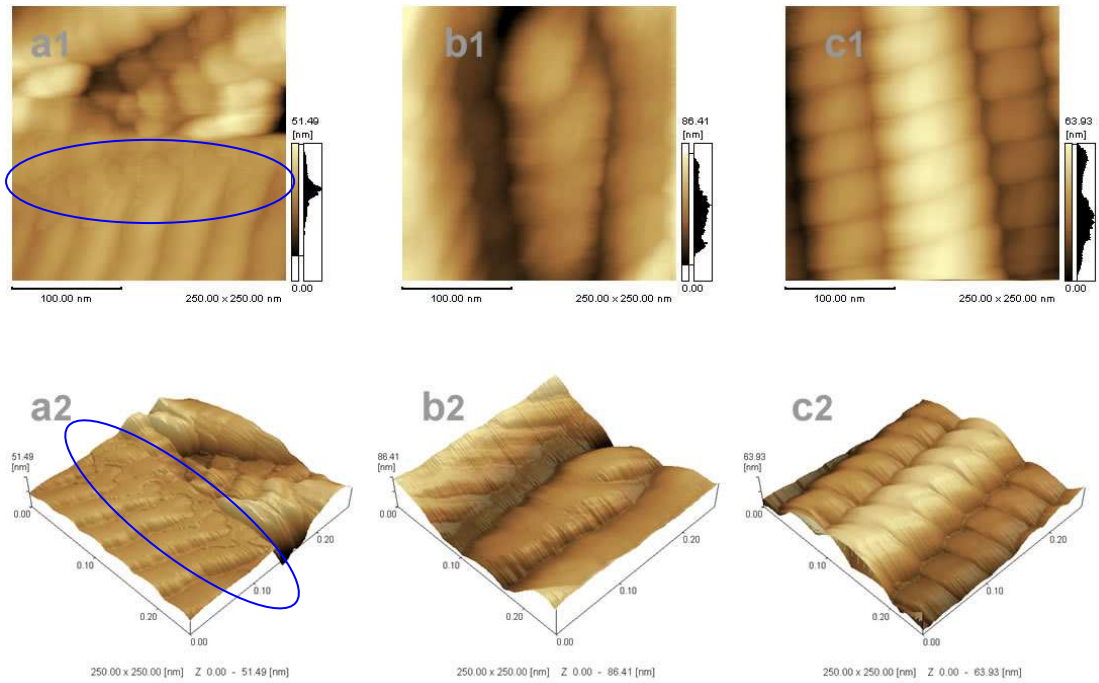


Fig. 4 AFM images for fat liquored leathers

(Microwave intensity: a1, a2 as 0W/L; b1, b2 as 8.13W/L; c1, c2 as 16.25W/L)

3.4 XRD analyses

Fig. 5 showed the X-ray diagrams for fat liquored 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^{o} and 21.2^{o}. As reported, the two peaks in the X-ray diagram of the collagen fiber in the hide/leather represent the side-chain distance peak (Peak 1) and the backbone reflection peak (Peak 2) [19-21]. 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.

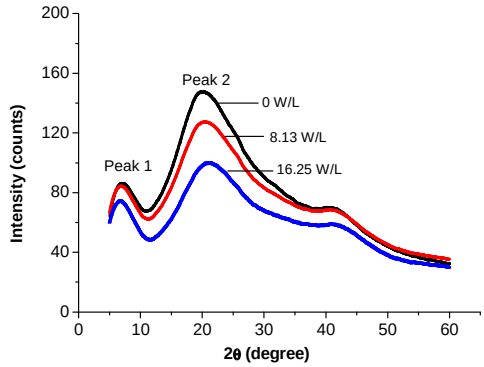


Fig. 5 X-ray diagrams for fat liquored leathers

3.5 Properties of fat liquors

The dielectric constants (ε) for fat liquors were indicated in Fig. 6. The ε values were higher than a level of 10^3, whether the fat liquors were heated with water bath or with microwave irradiation. The counter ions in the double-layer of the fat liquor colloidal particles migrated resulting in a surface capacitance and a magnified 'apparent' dielectric constant. These findings were similar to the dielectric constants for the suspensions of colloidal particles in aqueous electrolyte solutions reported by Marshall Fixman [22].

Fig. 6 also demonstrated that the dielectric constants were higher for the fat liquors 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.

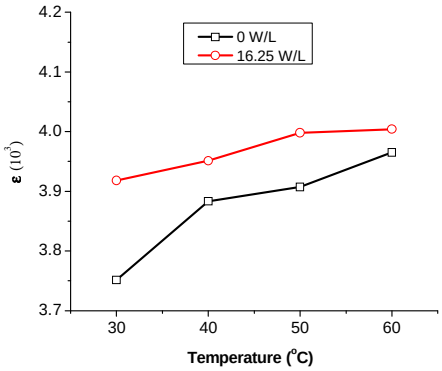


Fig. 6 Dielectric constants for fat liquor solutions
(Mass content as 1%; '0W/L' represented heating with water bath; '16.25W/L' represented preparing with microwave irradiation.)

As displayed in Fig. 7(a), the viscosity for the fat liquors 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 fat liquor particles

decreased with the rising temperature, and it fell rapidly by microwave irradiation (Fig. 7(b)). As we know, both of the viscosity and average size for the fat liquor particles would affect the penetrability and filling ability of fat liquors. The variations in fat liquor 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.

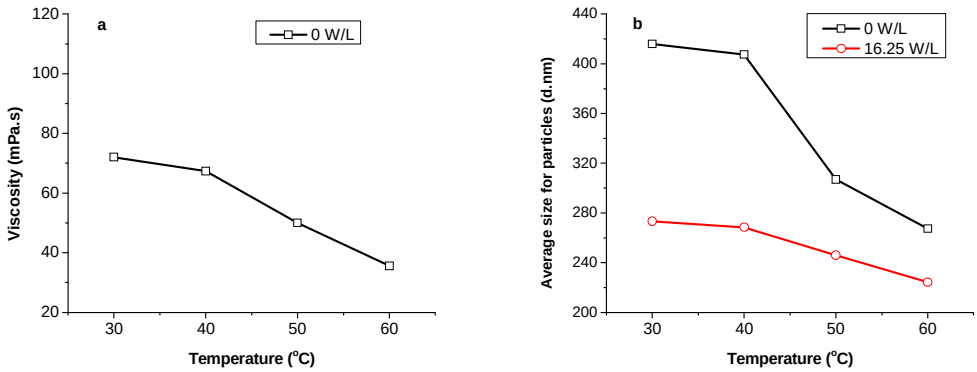


Fig. 7 Physical chemical properties of fat liquors

('0W/L' represented heating with water bath. '16.25W/L' represented preparing with microwave irradiation. (a) viscosity of the original fat liquors; (b) average size for the particles in 0.5% (mass content) fat liquor solution.)

3.6 Discussions

The temperature of leather increased by microwave radiation, which confirmed the presence of the '***heating effect***' of microwave field. Furthermore, some other phenomenons were found for both fat liquored leathers and fat liquors: (1) the microstructure of both collagen and collagen fibers would not vary distinctively; (2) both the viscosity and the average size of particles for the fat liquors decreased sharply, which would be helpful for the migration of oils and their uniform distribution. The variations for fat liquors elaborated the rise in softness after the fat liquored leathers were irradiated with microwave. What is more, the dielectric constants for the fat liquors increased rapidly by microwave exposure, which would further strengthen their response to microwave effects (including ***heating effect***) and promote their flowing accompanying with more even distribution of other leather chemicals. In a word, the distribution uniformity of leather chemicals in leathers could be effectively improved and the softness of leathers was elevated by microwave radiation.

4. Conclusions

Several techniques were exploited to characterize the variations in the microstructure of fat liquored leathers and the distribution of oils with microwave radiation (intensity lower than 16.25W/L), including scanning electron microscope, atomic force microscope and X-ray diffractometer. The results show that: (1) As for fat liquored leathers, there was 'heating effect' caused by microwave irradiation. Free moisture and capillary moisture in leather were firstly removed when exposed to a microwave field. What is more, there was scarce variation

in the thermostability of leather. (2) Microstructure analysis results indicated that the dispersion of the collagen fibers and the characteristic D-periodicity and crystallinity for the collagen were not damaged with microwave radiation. (3) There was some improvement in the softness for the leathers fat liquored with sulfited fish oil, after the leathers were exposed to a microwave field. The dielectric constants for the fat liquors increased in a microwave field, the viscosity of the fat liquors and the average size for their colloidal particles fell, both of which could facilitate the migration of oils in the leather leading to even distribution of leather chemicals.

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