THE INFLUENCE OF MICROWAVE DRYING ON LEATHER PROPERTIES

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The microwave irradiation and oven were used to dry goat garment leather crust, then the influence of different drying method on leather was compared by testing the mechanical properties, shrinkage temperature, softness, microstructure, dielectric constant and the uniformity of chrome tanning agent and fatliquoring agent. The results indicated that microwave drying would not damage the collagen structure, however the shrinkage temperature, softness and mechanical properties of microwave dried leather were improved, and the uniformity of chrome tanning agent and fatliquoring agent were also promoted. Moreover, the higher dielectric constant of microwave dried leather was observed compared with traditional dried leather together with much more order and dispersive arrangement of collagen weaving. The difference between microwave dried leather and oven dried leather proved not only thermal effect but also non-thermal effect existed during microwave drying process which could promote the interaction and combination between collagen and polar chemical materials. These effects both had positive contribution to leather comprehensive properties.

Keywords: microwave drying, leather comprehensive property, non-thermal effect

INTRODUCTION

Microwave is a fast, time and energy saving heat resources with the remarkable advantage of selective heating ability, so it had been used to dry leather and leather coat (Gilet, 1987; Komanowsky, 1990; Zhang *et al*., 2013). Several models were established to explain the kinetics of leather microwave drying to understand and utilize microwave in the process efficiently and systematically (Monzó-Cabrera *et al*., 2000, Monzó-Cabrera *et al*., 2001; Monzó-Cabrera *et al*., 2004). The difference between chrome tanned leather and vegetable tanned leather with various fat contents under microwave was found to be the primary evidence that microwave had extra effect more than thermal (Bajza, 1997).

Microwave could improve the leather color rub fastness (Gong *et al*., 2011) and fat distribution uniformity without damaging the leather (Gong *et al*., 2012). The chrome tanning process assisted by microwave irradiation could increase the shrinkage temperature of wet blue and improve the tear strength (Wang *et al*., 2011). These researches had proven the microwave had effect besides thermal also existed in leather making process with microwave, it was non-thermal effect.

Microwave was used in leather drying, but the detail influence of microwave on leather properties had not been studied yet except the microwave would not damage the leather. In this paper, the comparison on chemical and mechanical properties between microwave dried leather (MDL) and oven dried leather (ODL) were studied to clarify the thermal and non-thermal effect in microwave drying and the influence on leather properties, and provide reference for using microwave in leather industry further.

EXPERIMENTAL

Materials

The goat wet blue with the thickness of 1.0±0.1mm was prepared in the lab and finished retanning, neutralizing, dyeing and fatliquoring according to conventional garment leather process to get wet crust. The chemicals used for leather manufacturing were commercial grade and used for analyzing were research grade.

Leather Sampling and Drying Method

The wet crust was divided into two pieces along the spine after 12h standing, one was used for microwave drying which was cut as 30×30cm samples from belly and back respectively, the other one was used for oven drying with the same sampling method at the symmetric position.

The weight of each sample before drying was recorded and the water content was estimated about 80% (based on the total weight, and all water content mentioned in the paper was illustrated as the same). A MCR-3S microwave reactor (Xi'an Yuhui instrument Co. Ltd. China) was used for MDL drying with the 100W heating power, the leather sample was heated 2min every 2min to prevent high temperature at the beginning to damage the leather. The ODL was dried in a DHG-9070A drying oven (Shanghai Feiyue instrument Co. Ltd. China) at 45°C. The drying was stopped when the water content reduced to 20%. Then the MDL and ODL samples were placed into a temperature humidity chamber with 25°C and 65% relative humidity for 24h.

Test Methods

Physical Properties and Shrinkage Temperature (Ts) Measurement

Both MDL and ODL samples were conditioned as the standard method before mechanical properties testing. The mechanical properties like tensile and tear strength were tested by tensile machine (AI-7000S), and the softness was tested by measuring apparatus for leather softness (GJ9E1) according to standard. The shrinkage temperature was tested by Shrinkage Temperature Tester (MSW-YD4, China) according to standard.

Chrome Content and Chrome Uniformity Measurement

The samples were split into 3 uniform layers (about 0.3mm) and cut into about 1×1mm fragments, then dried in 102±2°C for 6h to constant weight. Each sample was digested with HNO_3 and H_2O_2 and the total chromium content in digestion solution was determined by Optima 2100DV Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) following the manufacturer's direction and the content of Cr_2O_3 in leather was calculated. Each value was an average of two tests. The uniformity of chrome distribution was calculated as following formula:

$$\text{chrome uniformity}(\%) = \frac{2 \times \text{Cr2O3 in middle layer}}{\text{Cr2O3 in grain layer} + \text{Cr2O3 in fresh layer}} \times 100\% \quad (1)$$

Fat Content and Fat Uniformity Measurement

The constant weighted leather fat content was determined by extraction with dichloromethane. The uniformity of fat distribution was calculated as follows:

$$\text{fat uniformity}(\%) = \frac{2 \times \text{fat in middle layer}}{\text{fat in grain layer} + \text{fat in fresh layer}} \times 100\% \quad (2)$$

Scanning Electron Microscope (SEM) Measurement

A JSM-5900LV scanning electron microscope (Japan) was used for the analysis. The micrographs for the leather cross sections were obtained by operating the SEM at low vacuum (10^{-4}Pa) with an accelerating voltage of 20kV at 1000 magnification levels.

Dielectric Constant Measurement

The 35mm×35mm samples were cut from MDL and ODL and a DZ5001 dielectric constant meter (China) was used for the test at 1MHz frequency level according to manufacturer's advice.

RESULTS AND DISCUSSION

Influence of Microwave Drying on Leather Mechanical Properties and Softness

Table 1. The mechanical properties and softness of ODL and MDL

Sample	Tensile strength: MPa		Tear strength: N/mm		Softness: mm	
	Back	Belly	Back	Belly	Back	Belly
MDL	25.65	21.50	56.52	38.64	6.69	8.91
ODL	23.10	20.10	55.13	36.51	6.23	8.30

As shown in Table 1, the tensile strength, tear strength and soft of MDL were slightly better than ODL, indicating the microwave had positive effect on leather mechanical properties and softness. Because water has much better absorptive capacity of microwave than leather itself, the drying rate of microwave slows down at the end of drying process with the leather moisture reducing obviously. In addition, there is no temperature gradient during microwave heating, leading the uniform water evaporation at the inner and surface of leather while the surface would be over-dried due to oven drying process is outside-in. The characteristics of microwave drying would not make the collagen fiber adhesion to prevent the stress concentration. These effects improved leather mechanical properties and softness.

Influence of Microwave Drying on Leather Shrinkage Temperature

Table 2. The shrinkage temperature of ODL and MDL

Sample	Back Ts: °C	Belly Ts: °C
MDL	116.0	114.4
ODL	114.1	113.5

Table 2 demonstrated the Ts of MDL back and belly were 1.9°C and 0.9°C higher than ODL respectively. The higher shrinkage temperature means better hydrothermal stability and better crosslink between collagen and tanning agents. It could infer that microwave improved the crosslink degree of leather as a result of the polar chromium complex molecules and active amino acid residues in collagen were affected by the high frequency conversion microwave electromagnetic field, then the extra collision, turn and oscillate between molecules except for temperature happened to accelerate the reaction rate and degree.

Influence of Microwave Drying on Chrome and Fat Migration

Table 3. Chrome uniformity and fat uniformity of ODL and MDL

Sample	Chrome uniformity: %		Fat uniformity: %	
	Back	Belly	Back	Belly
MDL	80.60	85.18	63.04	82.32
ODL	56.32	82.31	39.75	64.61

The chrome uniformity of MDL samples were much more even than ODLs, especially the back was 24.28% higher than the control (showed in Table 3). High chrome uniformity represents low difference of chrome content between inner and surface of leather. The better chrome uniformity of ODL was caused by the no temperature gradient and fast heating of microwave which could mostly avoid the migration of free and weak combined chromium with water evaporation to the surface occurred in the oven drying. Moreover, the crosslink between collagen and chrome promoted by microwave would reduce the content of free and weak combined chromium and decrease the potential of its migration.

Table 3 also indicated the microwave drying could get better fat uniformity leather. Prior study had verified that microwave could decrease the viscosity and particle size of fatliquoring agent to increase the permeability, leading fat was well dispersed during microwave drying. As fatliquoring agent uniform existed in leather, it could lubricate fibers sufficiently to get a better softness and improve the mechanical properties of leather.

Influence of Microwave Drying on Leather Microstructure

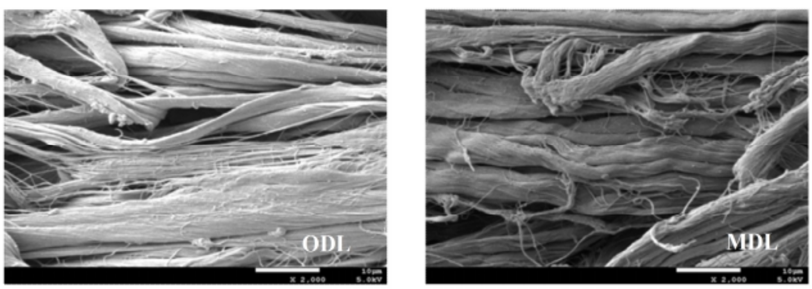

Figure 1. The SEM images of MDL and ODL back (A: MDL, B: ODL)

According to Figure 1, there was no significant difference between ODL and MDL in collagen weaving condition, but collagen fiber of MDL with a slight improvement in dispersity and orderliness. Collagen has diamagnetic anisotropy which trends to form a parallel arrangement which is perpendicular to magnetic field. The polar groups in collagen were affected by microwave electromagnetic field during drying process, then the groups with same charge had tendency to form parallel arrangement, leading repulsion force generation. So the tight section of leather such like butt and back had better dispersion and orderliness after microwave drying than traditional.

Influence of Microwave Drying on Leather Dielectric Constant

Table 4. The dielectric constant of MDL and ODL

Sample	Back	Belly
ODL	1.82	1.55
MDL	2.06	1.69

Table 4 presented the dielectric constant of leather at different sections. The MDL dielectric constant was higher than DOL, which was a direct proof of the non-thermal effect existing in microwave drying process because of the leather polarity increasing during the process. The induced dipole moment of polar molecule like collagen, tanning agent and fatliquoring agent produced with microwave electromagnetic field, making leather polarity increase to enlarge the dielectric constant.

CONCLUSIONS

The microwave drying would not damage the collagen structure; however, the leathers with higher shrinkage temperature together with better mechanical properties and softness were obtained comparing with oven drying. Moreover, the higher dielectric constant of microwave dried leather was observed compared with traditional dried leather together with much more order and dispersive arrangement of collagen weaving, The difference between microwave dried leather and oven dried leather proved both uniform thermal effect and non-thermal effect existing during microwave drying process; they have both positive contributions to leather comprehensive properties.

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REFERENCES

Bajza, Z. (1997), “The influence of fatliquor concentration on microwave drying kinetics”, *Journal of the Society of Leather Technologists and Chemists*, 81, 227-230.

Gilet, J. (1987), “Drying without heat”, *Journal of the American Leather Chemists Association*, 82, 61-64.

Gong, Y., Cheng, K., Zhang, T. and Chen W.Y. (2011), “Automated Clean Leather Dyeing Assisted by Wringing, Ultrasound and Microwave”, *Journal of the American Leather Chemists Association*, 106, 127-132.

Gong, Y., Zhang, T. and Chen W.Y. (2012), “Behaviour of fatliquored leather in a microwave field”. *Journal of the American Leather Chemists Association* , 107, 60-67.

Komanowsky, M. (1990), “Drying of leather with microwaves”, *Journal of the American Leather Chemists*

Association, 85, 131-141.
Monzó-Cabrera, J., Catalá-Civera, J. M., Plaza-González, P. and Sánchez-Hernández, D. (2004), “A model for microwave-assisted drying of leather: Development and validation”, *Journal of Microwave Power and Electromagnetic Energy*, 39, 53-64.
Monzó-Cabrera, J., Díaz-Morcillo, A., Catalá-Civera, J.M. and Delos-Reyes, E. (2000), “Heat flux and heat generation characterization in a wet-laminar body in microwave-assisted drying: An application to microwave drying of leather”, *International Communications in Heat and Mass Transfer*, 27, 1101-1110.
Monzó-Cabrera, J., Díaz-Morcillo, A., Catalá-Civera, J.M. and Delos-Reyes, E. (2001), “Effect of dielectric properties on moisture leveling in microwave-assisted drying of laminar materials”, *Microwave and Optical Technology Letters*, 30, 165-168.
Wang, H., Chen, W.Y., Gong, Y. and Sun, H.B. (2011), “Based on the studies of chrome tanning chemistry with microwave”, *Leather Science and Engineering*, 21, 10-14.
Zhang, C.L., Teng, B. and Chen, W.Y. (2013), “Effect of microwave drying on properties of leather coating”, *Leather Science and Engineering*, 23, 12-14.