

# The Influence of Microwave Non-thermal Effect on Leather Properties in Drying

by

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## Abstract

In order to study the influence of microwave, especially non-thermal effect, on leather properties, the microwave was used to dry leather together with the oven dried leather as a control. The back, butt and belly of dried leathers were tested for mechanical properties, softness, shrinkage temperature, chrome and fat migration, microstructure and dielectric constant. The results showed that microwave could improve the mechanical properties, softness and shrinkage temperature as a visible non-thermal effect. The non-thermal effect could also promote uniformity of chrome tanning agent and fatliquoring agent in leather and strengthen combination of these materials with collagen. In addition, the fiber weaving of microwave dried leather was more orderly and porous proved by SEM and XRD. Furthermore, the dielectric constant of microwave dried leather was higher than control, showing a direct proof of non-thermal effect for microwave. To sum up, Microwave in leather drying has not only thermal effect but also non-thermal effect on improving leather overall performance.

## Introduction

The electromagnetic wave with wavelength between 1mm and 1m is called microwave. The heat is generated by molecular friction of polar molecules such as water and alcohol under a changing electric and magnetic field of microwave.<sup>1</sup> As it is quite different from traditional heating like convection and conduction, microwave heating is a fast, even and energy saving process without temperature gradient in materials.<sup>2</sup> Drying is an important process in leather making in which the dried leather has the final collagen fiber matrix, feeling and performance. Hanging, toggling, pasting and vacuum are common drying methods. The moisture in the drying is removed by heated medium through convection, conduction and radiation.<sup>3</sup> These

methods might result in the hardening and shrinking phenomena of leather. Compared with a traditional procedure, microwave drying could overcome some defects of leather.<sup>4-6</sup>

As microwave was widely used in leather drying, several models were established to explain the process under microwave in static and dynamic.<sup>7,8</sup> The reasons why microwave could cause uniform water distribution and selective heating were also demonstrated in detail.<sup>9-12</sup> All the results validated that microwave could accelerate the drying process without damaging leather structure. Moreover, there was a study which found the leather with different fat content had different drying rate and process under microwave,<sup>13</sup> at the same time, the microwave could decrease the fatliquoring emulsion viscosity and particle size compared with water bath heating at same temperature.<sup>14</sup> These results indicated microwave has an extra effect beyond thermal, which could be called non-thermal effect. Some studies have proven the existence of non-thermal effect, such as microwave could improve the shrinkage temperature and tear strength of chrome tanned leather and promote color fastness of dyed leather.<sup>15,16</sup> Also, microwave could improve the cold tolerance of leather coating.<sup>17,18</sup>

The previous researches had illustrated the thermal effect of microwave on leather drying rate but the effects of microwave drying, especially the non-thermal effect, on leather chemical and physical properties has not been demonstrated yet. The water, tanning agents, fatliquoring agents and collagen in leather are polar materials. As the water could absorb microwave to evaporate and other non-volatile molecules could be affected by microwave, some special interactions between chemicals and collagen would be emerged, which may not exist in a traditional heating. In this study, the differences between microwave dried leather (MDL) and oven dried leather (ODL) were compared to get the effect of microwave drying on leather properties in detail, and provided some evidences to clarify non-thermal effect in the process.

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## Experimental

### Materials

The cattle wet blue with the thickness of  $1.5 \pm 0.1$  mm was prepared in the lab and finished retanning, neutralizing, dyeing and fatliquoring according to a conventional shoe upper leather process to get wet crust. The chemicals used for leather manufacturing were commercial grade and for analyzing were research grade.

### Leather Drying Process

The wet crust was cut into two pieces along the backbone; one half was used for microwave drying and the other half for oven drying.  $30 \times 30$  cm pieces were sampled from butt, belly and back respectively.

The weight of each sample before drying was recorded and the water content was estimated about 80% (based on the total weight). A MCR-3S microwave reactor (Xian 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 Experimental instrument Co., Ltd. China) at  $45^\circ\text{C}$ . The drying was stopped when the water content was reduced to about 20%. Then the MDL and ODL samples were conditioned in a constant temperature humidity chamber at  $25^\circ\text{C}$  and 65% relative humidity for 24h.

### Testing Methods

#### Mechanical Properties

Both MDL and ODL were conditioned as a standard method before mechanical properties testing.<sup>19</sup> The mechanical properties like tensile and tear strength of leather were tested by AI-7000S tensile machine (GOTECH testing Machines Inc. China),<sup>20, 21</sup> and the softness of leather was tested by measuring GJ9E1 apparatus (GOTECH testing Machines Inc. China) following a standard method.<sup>22</sup>

### Shrinkage Temperature (Ts)

The shrinkage temperature was tested by MSW-YD4 Shrinkage Temperature Tester (China) with the bath of glycerin solution (75%). Each value was an average of two samples which were along and across the backbone. Before testing, the samples were soaked in water 2h to rewet.

### Chrome Content and Distribution

The samples were split into 5 uniform layers (about 0.3mm) and cut into about  $1 \times 1$  mm pieces, and then dried in  $102 \pm 2^\circ\text{C}$  for 6h to constant weight. Each sample (about 0.150g) was digested in a flask with 10mL  $\text{HNO}_3$  and 5mL  $\text{H}_2\text{O}_2$  at heating condition for 30min. After cooling down, the digested solution was dissolved in a volumetric flask (100mL). The total chromium content in digestion solution was determined by Optima 2100DV Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, PerkinElmer, America) following the manufacturer's direction. The content of  $\text{Cr}_2\text{O}_3$  in leather was calculated.<sup>23</sup> Each value was an average of two tests. The uniformity of chrome distribution was calculated as following formula:

$$\text{Uniformity (\%)} = \frac{4 \times \text{Cr}_2\text{O}_3 \text{ in Middle layer}}{\text{sum of Cr}_2\text{O}_3 \text{ in other four layers}} \times 100\%$$

### Fat Content and Distribution

The samples were split into 5 uniform layers (about 0.3mm) and cut into about  $1 \times 1$  mm pieces after dried in  $102 \pm 2^\circ\text{C}$  for 6h to constant weight. Then the fat content was determined by extraction with dichloromethane.<sup>24</sup> The uniformity of fat distribution was calculated as following formula:

$$\text{Uniformity (\%)} = \frac{4 \times \text{fat in Middle layer}}{\text{sum of fat in other four layers}} \times 100\%$$

### Scanning Electron Microscope (SEM)

A JSM-5900LV scanning electron microscope (Japan Electronic Co. Ltd., Japan) was used for getting the images of leather cross section by operating the SEM at low vacuum with an accelerating voltage of 20kV at 1000 magnification level.

**Table I**  
Mechanical properties of ODL and MDL\*.

Sample	Tear strength (N/mm)			Tensile strength (Mpa)			softness (mm)		
	back	belly	butt	back	belly	butt	back	belly	butt
ODL	63.3	39.0	62.2	11.6	7.7	20.0	4.57	5.75	3.95
MDL	65.9	41.2	65.8	12.5	8.2	22.5	4.79	6.65	4.59

\*Each value was an average of two tests and the samples were perpendicular and parallel to the backbone.

### X-ray Diffraction Scanning (XRD)

The 20mm×20mm samples were cut from back of MDL and ODL and EMPYREAN X-ray diffraction scanning meter (PANalytical B.V., Netherland) was used for the test, and x-ray diffraction spectrograms were recorded.

### Dielectric Constant

The 35mm×35mm samples were cut, and a DZ5001 dielectric constant meter (Nanjing Dazhan instrument Co., China) was used for the test at 1MHz frequency level. The capacitance ( $C_2$ ) of sample and the distance ( $d$ ) between two plate electrodes were recorded when the electrode was connected with the binding post and the circuit resonance was adjusted to the maximum. The control capacitance ( $C_1$ ) was tested later when the distance between the two plate electrodes was same as testing the sample and circuit resonance was adjusted to the maximum too. The dielectric constant ( $\epsilon$ ) was calculated as  $\epsilon = (C_2 - C_1) \times \Phi^2$  and the results were the average of three tests.  $\Phi$  is the diameter of plate electrode (3cm).

## Results and Discussion

### *Influence of Microwave Drying on Leather Mechanical Properties*

Table I indicates that the softness, tear strength and tensile strength of MDL are better than ODL in each part, showing microwave having positive effects on leather softness and mechanical properties. Under microwave, the distance between fibers is larger than control as the area decreasing of MDL is less than conventional,<sup>5,6</sup> leading the stress concentration eliminating to improve the mechanical properties of leather. Moreover, with the moisture reducing in drying, the microwave drying rate slows down obviously<sup>11</sup> to prevent the over drying and fiber bonding at the end of the process, this benefits for the softness and mechanical properties too.

### *Influence of Microwave Drying on Leather Shrinkage Temperature-The Indirect Evidence of Non-thermal Effect*

As shown in Table II, the shrinkage temperature of MDL back, butt and belly are 1.4, 0.8 and 1.5°C higher than ODLs respectively. Although the  $T_s$  increasing is not very significant, it could still demonstrate the leather hydrothermal stability improved by microwave. Under microwave, the polar molecules like chrome tanning agent and collagen have extra energy to turn and oscillate to enhance probability of effective collision, so the combination between collagen and unstable chromium agents is promoted to get higher shrinkage temperature. This effect is not caused by temperature. This may belong to a non-thermal effect. Some studies found microwave could reduce the active energy of reaction,<sup>25,26</sup> so it could be inferred that the active energy reducing might lead to the chrome tanning degree improving. The  $T_s$  increase of MDL should attribute to microwave non-thermal effect.

### *Influence of Microwave Drying on Solute Migration – The Indirect Evidence of Non-thermal Effect*

It could be found in Table III that the chrome and fat uniformity of MDL in butt, back and belly are much better than ODL corresponding areas, especially at belly. The oven heating is from outside-in due to temperature gradient, leading the surface water evaporating at first, then inner water migrating to the surface. In this way, some unstable combination materials could migrate to the surface with water, resulting in an uneven distribution of chrome and fat. However, microwave is a volume heating from inside-out without temperature gradient, so it promotes the uniformity of fat and chrome in the leather further.

The microwave could reduce the viscosity and particle size of fatliquoring emulsion through high frequency turn and oscillation caused by the interaction between electromagnetic field and charged emulsion particles.<sup>14</sup> This may result in a better fat uniformity. The better fat uniformity in leather could lubricate fibers evenly, which supports the results that MDL has better mechanical properties and softness.

### *Influence of Microwave Drying on Fiber Structure – The Indirect Evidence of Non-thermal Effect*

According to Figure 1, there is no significant difference between ODL and MDL in collagen state. But the fiber matrix of MDL is arranged orderly, in addition, the larger porous with less adhesion between fiber bundles are observed. The polar groups in collagen

**Table II**  
Shrinkage temperature of ODL and MDL.

Sample	Shrinkage temperature (°C)		
	back	belly	butt
ODL	110.7	106.9	115.2
MDL	112.1	108.4	116.0

**Table III**  
Influence of microwave on chrome and fat distribution.

Sample	Chrome uniformity (%)			Fat uniformity (%)		
	back	belly	butt	back	belly	butt
ODL	70.0	83.1	77.7	25.1	46.7	20.2
MDL	89.4	95.8	85.7	34.2	64.4	26.9

are affected by microwave electromagnetic field in drying, and the groups with same charge have trend to form a parallel arrangement, leading the lager porous and less adhesion.

Usually, there are two peaks for collagen XRD image, the one is  $2\theta$  peak at about  $7^\circ$ , representing the distance between molecular chains; the other one is  $2\theta$  peak at about  $23^\circ$ , corresponding to diffuse scatter of collagen.<sup>27</sup> The XRD image of ODL and MDL is shown in Figure 2. The two peaks of MDL are  $7.567^\circ$  and  $22.778^\circ$  respectively, and the two peaks of ODL are  $7.424^\circ$  and  $23.694^\circ$  respectively. The  $2\theta$  peak at about  $7^\circ$  of MDL is  $0.143^\circ$  higher than ODL, indicating the distance between collagen chains in MDL decreasing. Also, the  $2\theta$  peak at about  $23^\circ$  of MDL is  $0.916^\circ$  lower than ODL, showing the orderliness improving. This results are compared with the SEM image.

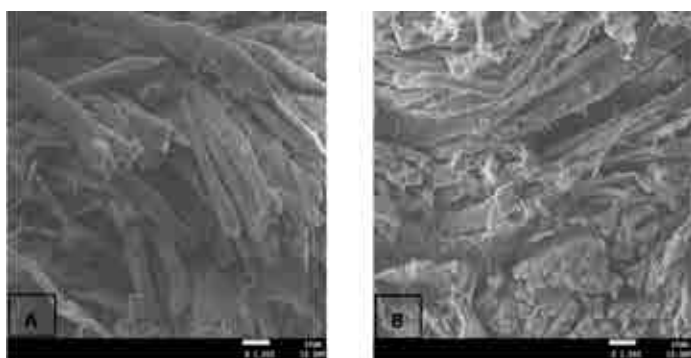


Figure 1. SEM images of leather in back A: MDL, B: ODL.

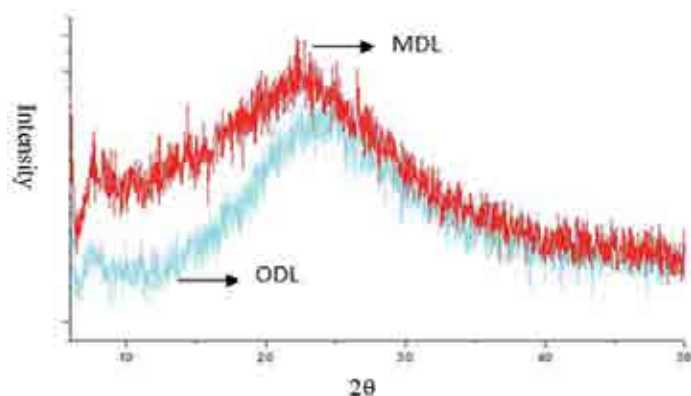


Figure 2. XRD image of collagen in leather back.

**Table IV**  
Dielectric constant of ODL and MDL.

Sample	back	belly	butt
ODL	3.15	3.08	3.66
MDL	3.52	3.48	3.93

### ***Influence of Microwave Drying on Leather Dielectric Constant – The Direct Evidence of Non-thermal Effect***

Table IV shows the dielectric constant of leather. The different parts of leather have a different dielectric constant, but the dielectric constants of each part of MDL are higher than ODLs. For a material, there is a positive correlation between dielectric constant and polarity. That is the higher dielectric constant the larger polarity. As the water content in the leather samples is same after a sufficient conditioning, the dielectric constant could represent the polarity of leather directly. Under microwave, the system dipole is not zero as the instantaneous dipole of nonpolar molecules and induced dipole of polar molecules while in a traditional heating the system dipole is always zero. The polar molecules in the leather have an induced dipole caused by microwave to enlarge the dielectric constant. This is a direct evidence of non-thermal effect in leather microwave drying.

There are two effects in microwave acting on substance, thermal and non-thermal. Thermal effect comes from medium absorbing microwave and converting into heat. Non-thermal effect refers to phenomena of system response for substance absorbing microwave energy, which could not belong to temperature changing. After wet end, huge amount of polar molecules in leather will be affected by microwave; in addition, microwave could also act on the polar groups in collagen, leading a faster molecular movement beyond temperature. As a consequence, the interactions between collagen and chemicals are different from a conventional heating. Therefore, not only thermal effect but also non-thermal effect could influence the leather properties in microwave drying.

## **Conclusions**

The differences between microwave dried leather and oven dried leather were compared in visible views such as mechanical properties, softness and shrinkage temperature and in chemical and structural views like chrome and fat uniformity, microstructure and dielectric constant. The results showed that microwave improved the mechanical properties and shrinkage temperature, the chrome and fat distribution uniformity and the porosity and orderliness of fiber matrix, which could indirectly prove the non-thermal effect in leather drying. Also, microwave increased the dielectric constant of leather, which could directly prove the non-thermal effect in the process. In brief, microwave could improve leather overall performance through not only thermal effect but also non-thermal effect in leather drying.

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