Chrome Tanning Process and the Leather Properties Under Microwave Irradiation

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Abstract. Some studies clarified that microwave strengthened tanning effect and made the leather have better thermal stability, but influence of microwave on tanning process and leather properties have not been elaborated in detail. For illustrating the influence of microwave on chrome tanning process, pickled skin was tanned for 6h as penetration procedure and then basified for another 4h as fixation procedure. The tanning under microwave irradiation (MW) was experimental sample and under water bath heating (WB) was control. UV-Vis, pH and ICP-OES were used to measure the changes of tanning effluent and leather chrome content during tanning. Shrinkage temperature meter, DSC and TG were used to determine the differences between MW and WB on aspect of thermal stability and resistance. SEM was applied to character how microwave affected leather structure compared with conventional heating. The results indicated microwave accelerated chrome tanning agent penetration and brought about higher chrome exhaustion. The leather tanned with microwave assisting had better hydrothermal and thermal stability as well as thermal decomposition property. However, the leather structure of MW, including h hierarchical structure, was same as WB. In sum, microwave had positive effect on accelerating tanning rate and resulting in better leather properties without any negative effect on leather structure. Therefore, microwave would be a potential choice for achieving clean and sustainable chrome tanning by making tanning much faster and more efficiency.

1 Introduction

Microwave is the electromagnetic wave with frequency between 300MHz and 300GHz, and the civil frequency of microwave in China is 2450MHz[1]. Microwave could accelerate chemical reaction rate, promote reaction yield and make some reactions happen under milder condition rather than high temperature and high pressure. Just as the characters, microwave is widely used to assist huge amount of chemical reactions[2,3]. The reason why microwave has positive effect on chemical reaction could be attributed to thermal effect and non-thermal effect. However, the kinetic[4], mechanism[5], activation energy[6] and pre-exponential factor of reactions[7] under microwave are changes, indicating non-thermal effect which is not relating to temperature increasing is unique effect of microwave to promote chemical reactions[8, 9].

In leather industry, microwave is used in many procedures, such as unharing and bating[10], dyeing[11], fatliquoring[12] and drying[13], in which microwave promotes the chemicals penetration into leather and results in more even distribution, in addition, the combination between collagen and chemicals is strengthened by microwave also[14]. In tanning aspect, microwave has more significant influence on chrome tanning liquor hydrolysis and olation compared with heated by conventional method[15,16]. For vegetable tanning liquor, microwave has positive effect on colloid stability and dispersibility[17]. Moreover, microwave could enhance tanning effect. When microwave was used to treat chrome well penetrated leather, the leather had higher Ts and better tear strength[18]. In vegetable tanning, microwave not only made leather have higher Ts but also resulted in better polyphenol exhaustion[19,20].

Furthermore, microwave made zirconium tanned leather have better thermal stability. These evidences suggest microwave has positive effect on tanning.

Chrome tanning contains relatively independent procedures, chrome tanning penetration and fixation, as hides or skins have certain thickness. The previous study demonstrated microwave could improve chrome tanning process and tanning effect by using hide powder[21]. However, the penetration and fixation procedures were not clear because of applying powdered tanning material. Hitherto, the influence of microwave on chrome tanning process, like tanning agent penetration rate and distribution during tanning, as well as how it affected leather properties had not been illustrated in detail. In this work, chrome tanning was undertaken with microwave heating (MW) and water bath heating (WB) respectively, and then the differences between the two samples on aspects of tanning liquor properties and chrome penetration were compared. Next, the thermal stability of leathers tanned under different heating was measured by Thermal Gravimetric Analyzer (TG) and Differential Scanning Calorimeter (DSC), and leather structure was characterized by Scanning Electron Microscope (SEM). The research would provide reference to apply microwave in chrome tanning process to achieve more effective tanning.

2 Experimental

2.1 Materials

Pickled goat skins were prepared according to conventional upper shoe leather process with thickness around 1.0mm. Chromium sulfate hexahydrate was from Shanghai Aladdin Reagents Company. Sodium bicarbonate and sodium chloride were purchased from Chengdu Kelong Chemical Ltd. Other chemicals were commercial grade for leather manufacturing and research grade for analysing.

2.2 Chrome tanning process stract

90.00±0.05 sodium chloride and 191.33±0.01g chromium sulfate hexahydrate were dissolved in 1400mL distilled water at first, then 10.714±0.002g sodium bicarbonate was dissolved in 1400mL distilled water and the solution was put in chrome solution within 30min under stirring, finally, the mixture was stirred for another 30min to obtain the chrome tanning liquor with 100g/L chromium sulfate and 33% basicity.

Pickled goat skin was cut into 2cm×6cm pieces. 140g skin pieces were tanned in a 1000mL beaker with 700mL chrome tanning liquor prepared above. The MW sample was heated by microwave at 40 °C with stirring and the WB sample was warmed by water bath heater at same condition. After 5h tanning, 1g sodium bicarbonate was added into the tanning system every one hour and repeated for 5 times. The total tanning time was 10 hours. The first 5 hours were regarded as penetration procedure and the last was fixation procedure.

The pH of both tanning liquors were measured every 1 hour by pH-3C pH meter (Shanghai Yidian Instruments Co., Ltd.), at the same time, 2mL tanning liquor was sampled for UV-Vis determination. Moreover, skins were taken out every 1hour for chrome content test and the shrinkage temperature measurements were carried out after 4h tanning and 10h tanning. The leathers were lyophilized when tanning was finished for other tests.

2.3 Testing methods

2.3.1 Ts measurement

The shrinkage temperature was tested by Shrinkage Temperature Tester (MSW-YD4, China) into the bath of 75% glycerine solution. Each value was an average of two tests.

2.3.2 Leather chrome content measurement

0.150±0.001g lyophilized leather was digested in a 100mL flask with 10mL nitric acid and 5mL hydrogen peroxide under boiling for 30min. After cooling down, the digested solution was dissolved in 100mL volumetric flask. The total chromium content in digestion solution was determined by Optima 8000DV Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, PerkinElmer, America) following the manufacturer's direction and then the content of Cr_2O_3 in hide powder was calculated.

2.3.3 UV-Vis determination

The tanning liquors were filtrated by using 0.22μm microporous membrane and then diluted ten times with distilled water. A UV1900 UV-Vis spectrometer (Beijing Puxi General Instruments Co., Ltd.) was used to scan the diluted solution from 350 to 650nm with the scanning rate of 120nm/min and wavelength (WL) interval of 1nm. The wavelength of the solution at about 420nm was named λ1, and the corresponding absorbance (ABS) was named A1. The wavelength of the solution at about 580nm was named λ2, and the corresponding absorbance was named A2. The R value was calculated as R=A1/A2.

2.3.4 DSC measurement

The dried leathers were put into Aluminium crucibles and heated by a DSC 200 PC differential scanning calorimeter (Germany) with heating rate 10 °C/min in a N_2 atmosphere (flow N_2: 100mL/min). The range of temperature was from 30 to 250 °C.

2.3.5 TG measurement

The dried samples were put into ceramic crucibles and heated by a NETZSCH TG 209 F1 thermal gravimetric analyzer (Germany) with heating rate 10 °C/min in a N_2 atmosphere (flow N_2: 100mL/min). The range of temperature was from 40 to 800 °C.

2.3.6 SEM observation

A JSM-7500F scanning electron microscope (Japan Electronic Co. Ltd., Japan) was used for observe leather cross section images by operating the SEM at low vacuum with 15kV accelerating voltage.

3 Results and discussion

3.1 Influence of microwave on chrome tanning process

Table 1. The influence of different heating method on chrome tanning process.

Time	WB			MW		
(h)	pH	R value	Cr_2O_3 content (mg/kg)	pH	R value	Cr_2O_3 content (mg/kg)
1	2.66	1.1856	7.96	2.64	1.1749	9.52
2	2.72	1.1970	12.16	2.70	1.1930	14.15
3	2.68	1.2015	15.84	2.65	1.1964	18.36
4	2.66	1.2038	18.26	2.62	1.2007	21.62
5	2.65	1.2044	20.02	2.62	1.2002	22.66
6	2.73	1.2119	21.62	2.70	1.2065	25.84
7	2.94	1.2392	29.79	2.89	1.2328	33.11
8	3.18	1.2595	35.23	3.16	1.2452	39.54
9	3.48	1.2981	39.56	3.44	1.2758	44.08
10	3.89	1.2942	41.88	3.83	1.2872	47.15

In Table 1, it could be found that the pH, R value of WB tanning liquors were always higher than MW under corresponding time in the whole chrome process. However, the leather Cr_2O_3 content of MW was larger than WB at same condition. Because microwave had more powerful effect on chrome complex hydrolysis and olation and resulted in lower pH, the lower pH of MW samples compared with WB indicated microwave also promoted chrome complex hydrolysis and olation[16]. In general, if there is bridge formed between chromium and ligands, the R value is larger than 1.19, and the more bridge the higher R value. The results of R value in Table 1 suggested that microwave might improve the combination between collagen large-size chrome complexes for causing lower R value, and the Cr_2O_3 content results also indicated same situation. Furthermore, the Cr_2O_3 content of MW always larger than WB indicated microwave promoted chrome penetration and combination during tanning. On the other hand, microwave-assisting could reduce tanning time but increase efficiency as less time was needed to achieve same chrome. In summarize, microwave had positive effect on chrome penetration and combination during tanning.

As chrome complexes and collagen were polar molecules, they were affected by microwave and generated additional movement style which had oscillation under electromagnetic field while the system under conventional heating only contained the movement caused by temperature. Therefore, molecule movement under microwave was more turbulent to benefit for chrome penetration, and higher possibility for the collision between collagen residue and chromium complex to produce better chrome exhaustion.

3.2 Influence of microwave on leather thermal stability

One of the most important tanning effects is strengthen the thermal stability of leather. In this part, the leather tanned under different heating methods was subjected DSC, TG and shrinkage temperature tests to clarify influence of microwave on chrome tanning effect. The DSC and TG results were were listed in Table 2.

Table 2. The influence of different heating method on leather thermal stability.

Sample	T_d (℃)	ΔH (J/g)	T_{max}(℃)	Carbon residue (%)	Ts(℃)
WB	98.5	351.2	350.5	19.57	103.0
MW	104.8	374.9	354.7	29.58	109.3

In DSC results, higher denaturation temperature (T_d) and greater energy-consuming during denaturation (ΔH) of MW sample were obtained. They indicated the collagen conformation of leather tanned under microwave was much more stable. In TG results, the maximum decomposition temperature (T_{max}) but less weightlessness between 200 °C and 600 °C which attributed to peptide decomposition during heating and could be used to represent collagen structure stability of MW were observed; in addition, more carbon residue of MW indicated there were more unviolated substances, such as chrome, in leather and much less collagen decomposed during tanning. They illustrated microwave-assisting during tanning improved leather thermal resistance. In Ts results, the terminal Ts of MW was 6.3 °C higher than WB. Moreover, the Ts of MW after penetration (tanning 6h) was 85.6 °C while the WB at same condition was only 73.5 °C (the results were not showed in Table 2). They showed microwave not only improved cross-linking effect but also made the effect work under lower pH.

Since there were more high-positive charge and molecular-size chromium complexes, which have better affinity to collagen and contribute to cross-link mainly, in tanning liquor under microwave irradiation, the combination between collagen and chromium complexes were strengthened, in other word, the tanning effect was stronger. On the other hand, just as microwave promoted other chemical reactions obviously, the cross-linking reaction between collagen and chromium was easier to emerge and the efficiency might be higher under microwave compared with water bath heating. No matter higher chrome exhaustion or better cross-link, microwave promoted chrome tanning effect and resulted in better thermal stability of leather.

3.3 Influence of microwave on leather structure

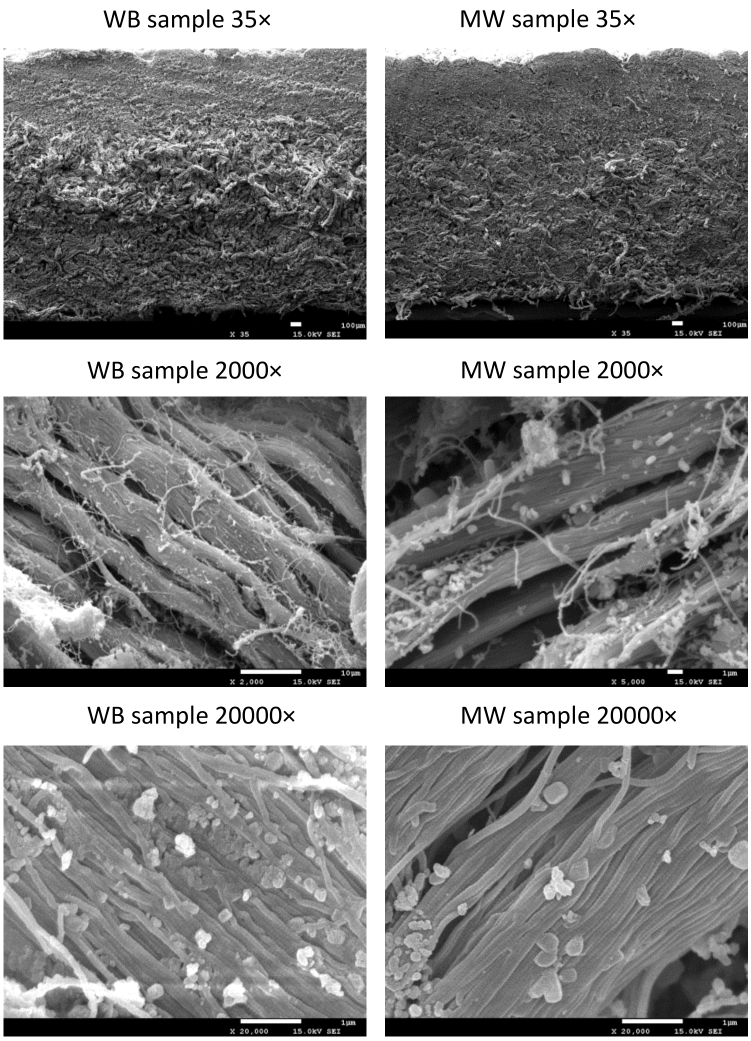

Fig. 3. SEM images of leather tanned under different heating method.

SEM was used to observe the morphologies of leather tanned under different heating method, and the images were shown in Fig. 3. When the magnification was 35, the cross section of two samples had clear interwoven flexuous fiber bundles network. With the increasing of magnification to 2000, the leather consisted of thin uniform fibers which packed together orderly and there was no significant difference between the two samples. Under magnification higher to 20000, collagen fibrils exhibited the alternative brightness and darkness, it attributed to the unique staggered by a quarter of collagen. Although microwave promoted chrome tanning process and effect, the hierarchical structure of leather remained as normal.

4 Conclusions

By comparing the differences on aspects of tanning process and leather performance between chrome tanning with microwave assisting and water bath heating, it could summarize as following: firstly, chrome tanning process under microwave irradiation was faster than traditional heating, so microwave would be an effective routine for accelerating chrome tanning process; secondly, the leather tanning with microwave assisting had better thermal stability, in other word, the tanning effect was promoted by microwave, thus, microwave could be used to innovate chrome tanning process for excellent performance leather; thirdly, the tanning process and effect were affected by microwave but collagen structure remained. In short, microwave has positive effect on chrome tanning process and leather performance.

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