Ti(III)-Tannin Combination Tanning Technology Based on Microwave Irradiation

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Abstract. Microwave is a fast, efficient and energy-saving thermal resource, hence an attempt has been made for applying this technology in the combination tanning using titanium (III) and tannin extracts. In this work, the microwave effects on the complex reaction of Ti(III) with tannin extracts and leather products properties were investigated. The precipitation condition was used to characterize the complexation degree between Ti(III) and tannin extracts. And the shrinkage temperature, tear strength, SEM, and histological structure were used to characterize the changes in the physical and chemical properties of the combined tanned leather. The results showed that microwave irradiation can accelerate the complex reaction of Ti(III) with tannin extracts. At the room temperature, the mixture of tannin and Ti(III) kept stable at pH 3-4. In addition, microwave could increase the shrinkage temperature, tear strength, and fibrage of Ti(III)-tannin tanned leather, and it would not change the combination mode of the skins with tanning agents as well as the hierarchical structure of collagen. Therefore, these results inferred that microwave could promote the reaction between Ti(III) and tannins and the combination of tannins with collagen, which may provide a theoretical basis for the application of microwave in Ti(III)-tannin combination tanning technology.

1 Introduction

Microwave is an electromagnetic wave with a frequency between 300MHz and 300GHz, which can excite the transition of the rotational energy level of the molecule, thereby directly acting on the condensed matter molecules in the reaction system. Because of its convenience, rapidity, homogeneity, simple operation to control, small pollution, and low energy consumption, microwave heating is attracting more and more attention from chemists all over the world.[1,3] A large number of experiments in recent years have confirmed that microwave could greatly increase the reaction rate of some chemical reactions.[4-8] Therefore, leather chemists and technologists have tried to apply it in leather making, such as fat-liquoring, dyeing, drying and so on[9,10], where there was a positive effect on the performance of leather products compared to conventional heating[11,12].

In recent years, as the environmental pressures have increased, various strategies and methods have been tried for leather industry to replace traditional tanning processes. The combination method with metal salt and vegetable tannin was reported as a practical to manufacture leather with 'chrome-like' properties[13], which may reduce the environmental pollution. Known by Covington[14], tannin extract and titanium sulfate (Ti(III)) could be used as a combination tanning agent and corresponding leather products with high thermal stability were obtained after the treatment by using this method. After that, Bo[15] analysed the complexation of Ti(III) and tannin extracts, and the results reported that the temperature, system pH, complexation ratio, and tannin addition order had a huge effect on the complexation reaction, and Ti(III)-tannin agent could increase the shrinkage temperature of the leather.

Owing to the polarity of collagen, tannin and Ti(III), their composition and properties perhaps have a change in the microwave electromagnetic field, which may lead to the change of tanning process, technology and even tanning mechanism. However, the related application of microwave in the Ti(III)-tannin combination process has not been reported yet. In this work, the microwave effects on the complex reaction of Ti(III) with tannin extracts and leather products properties will be investigated, in order to provide a theoretical basis for the application of microwave in Ti(III)-tannin combination tanning technology.

2 Experimental

2.1 Materials

Pickled sheepskin was made in our laboratory according to conventional technology[16]. Titanium sulfate (Ti(III)) was purchased from ShandongXiya reagent Co. Ltd. Acacia Mangium extract (AME), Valonia extract (VE), Bayberry extract (BE) were industrial products, commercially purchased from Wu Ming tannin extract factory in Guangxi, China. All the other compounds used were analytical reagents commercially purchased from Chengdu Kelon Chemical Reagent Factory, China. 0.01g/mL of Ti(III) solution and 0.02g/mL of tannin extract solution were prepared respectively. And the pH of the Ti(III) solution was adjusted to 1.40 with sulfuric acid.

2.2 Complex at Different Temperature

Mixtures containing 10 mL $Ti_2(SO_4)_3$ and 5 mL tannin extract solution were diluted to 30 mL with water. And then they were kept in different temperature conditions at 30, 40 and 50 °C for 2 h respectively under microwave irradiation heating (MIH, produced by a Xian Yuhui MCR-3 microwave chemistry reactor). Corresponding procedure under water bath heating (WBH) acted as a control. After being centrifuged for 0.5 h with 6000 r/min rotating speed, the precipitations were dried at 120°C, and weighted.

2.3 Mixture under Different pH

Mixtures were composed of 15 mL of the tannin extract solution (4 g/L) and 15 mL of Ti(III) solution (0.4 g/L), and neutralized to a serious pH (1, 2, 3, 3.5, 4, 5, 6 and 7) with dilute sulfuric acid or sodium bicarbonate ($NaHCO_3$). After that, the samples were placed at room temperature for 4 h, observing the solution precipitation condition.

2.4 Tanning with Different Tannin Extract and Ti(III)

Two pickled sheepskin pieces were sampled (13cmx7cm) along the backbone and weighted (the following reagent dosage: 1.5 times of the pickled pieces mass). 30% tannin extract, 400% water, 6% sodium chloride and 3% Ti(III) were added into a beaker and then the solution was neutralized to pH 3.0-4.0 with $NaHCO_3$. After the pH was stable, the skin sample (2cm×6cm) was put into the beaker, and the tanning was performed at room temperature. After the tannin extract had completely penetrated into the skins, the samples were taken out. One test was carried out for 12 hours at 50 °C under MIH for the experiment, and the other served as a control being treated by WBH. After the tanning finished, the sample was taken out and collected for test.

2.5 Microscopy of Ti(III)-tannin Tanned Leather

Tissue staining microscopy is one of the more effective techniques for observing the histology structure of the leather. 2cmx2cm pieces of the Ti(III)-tannin tanned leather were first fixed in 10% neutral formaldehyde solution (100mL, v/v) for 48 hours. Next, the fixed piece was washed completely and sectioned (thickness, 12µm) using a CM-1950 freezing microtome (Leica, Germany); after this step the section was attached to the slide with protein glycerin, and dried for 72 hours in air. At the staining step, the section was placed in the solution containing hematoxylin alcohol solution (1%) and ferric chloride solution (29%, 4mL) with 95 mL of distilled water for 20 min, and then washed and staining again in picric acid saturated aqueous solution containing 1% acid magenta solution (85:15, v/v) for 3 min, washed and followed by 2 min of differentiation with ethanol (95%) for three times, and immersion in 95% alcohol, pure alcohol and xylene, respectively (2 times each of the alcohol liquids and once for xylene, 2 minutes each time). The final stained piece was observed under the microscope. The magnification was 15×.

2.6 Measurement of Physical and Mechanical Properties

To determine the shrinkage temperature (Ts), a 2.5cm x 1.0cm leather piece was heated in glycerin solution at 2°C/min rate measured by a MSW-YD4 digital shrinkage temperature meter (Institute of Sunshine Electronics, Shaanxi University, China). The tensile and tear strength samples were conditioned at 20±2 °C (RH, 65±2%). The 4.5cmx1.0cm leather piece was measured with a thickness gauge and an AI7000S automatic tensile machine (GOTECH testing Machines Inc., China) was used for the tests. The tear strength was calculated using Formula 1:

$$T=F/t \qquad (1)$$

where T is tear strength (N/mm), Fistear force (N) and t is average thickness of the sample (mm).

2.7 Measurement of Scanning Electron Microscope (SEM)

The cross-sections of the tanned leather were examined in a Jeol JSM-7500F scanning electron microscope. The samples were coated with a gold film before such measurement.

3 Results and Discussion

3.1 The Influence of Microwave Temperature on the Complexation

The precipitation amounts of the complexation under different temperature were shown in Table 1. Apparently, in the condition of both of MIH and WBH, the precipitation amounts were increased with the temperature, indicating that the complexation of the tannin with Ti(III) solution was enhanced as the temperature went up. However, MIH method promoted the reaction more strongly. From 30°C to 50°C, the precipitation amounts of the microwave group were 1.0 mg, 8.1 mg and 17.6 mg, respectively, which were more than that of control. It could be inferred that microwave had an ability to increase the collision of tannin particles and Ti3+, which made the complexation easier.

Table 1. The precipitation amounts of the complexation under different temperature.

Temperature (℃)	Precipitation amounts (mg)	
	MIH	WBH
30	6.6	5.14
40	31.2	23.1
50	68.4	50.8

3.2 The Influence of pH on the Stability of The Tannin and Ti(III) Mixed Solution

It can be seen from Fig. 1 that the mixed solution becomes cloudy immediately at pH 1 and 2, because pH deviates from the isoelectric point of tannin, the phenolic hydroxyl group reacted rapidly with Ti^{3+}. At pH 3 and 4, there is no precipitation in the mixed solution, thus the solution is stable, which may be because the phenolic hydroxyl of the tannin extract was hidden, and the tannin could not react with Ti^{3+}. Due to titanous sulfate is hydrolyzed to form precipitation at pH 5, 6, and 7, there are some white precipitates in the mixed solution. As it is shown from Fig. 2, the mixed solution is still clear and stable at pH 3, 3.5 and 4.0 after standing for 4 h. So, we could conclude that the complexation reaction is slow at pH 3-4 at room temperature.

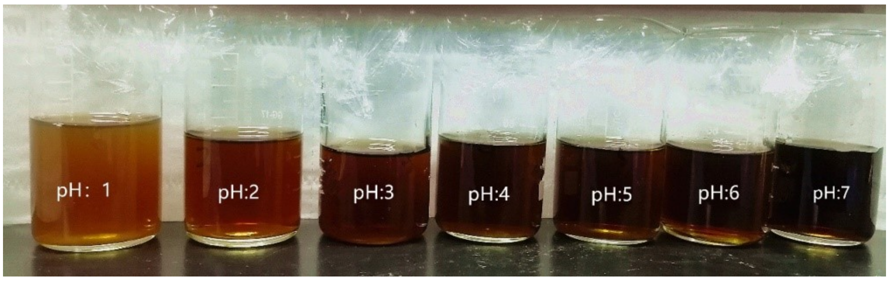

Fig. 1. The mixture of tannin and Ti(Ⅲ) under different pH.

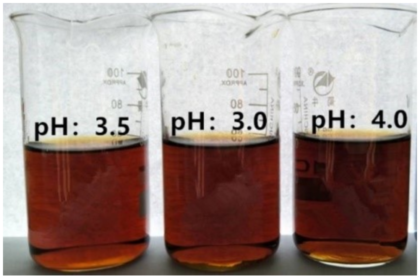

Fig. 2. The mixture of tannin and Ti(III) at pH 3.0, 3.5 and 4.0.

3.3 Histology Structure Analysis

The fibrous structure can be observed though the microscope. Fig. 3 is the histology structure of Ti(III)-tannin tanned leather. It can be found that the fibers of the experimental are closer and more evenly distributed than the control. The reason of this phenomenon could be explained by that the interaction of Ti^{3+}, tannin and collagen was accelerated in the microwave high frequency transformed electromagnetic field, thus making the crosslinking is more intense. Besides, because of the bulk-heating of the microwave, the collagen fibers' weave was more uniform.

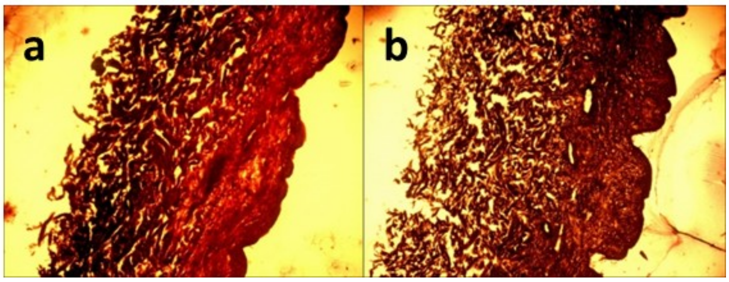

Fig. 3. The fibrage of the leather tanned underWBH (a) and MIH (b)(15×).

3.4 Ts Analysis

Table 2 shows Ts of the leathers obtained using different tanning processes. It can be seen from the Table 6 that both microwave heating and water bath heating methods can increase the Ts of the leather. Ts of the leather tanned under MIH was greater than that of WBH. Among the three types of tannin, Ts of VE tanned leather was most obviously improved, which increased by 5.6 °C after microwave heating. For BE tanned leather, the microwave promotion effect showed a little, and the Ts of the microwave group was only 1.2 °C higher than that of control. However, no matter what the tannin type is, the Ts could be increased under MIH. This may be because the microwave could not only promote the combination of tannin and Ti^{3+} with collagen, but also enhance the combination of tannin and Ti3+, strengthening the crosslinking effect among tannin, Ti^{3+}, and collagen, producing a synergistic effect of tannin and Ti^{3+}.

Table 2. The Ts of Ti(III)-tannin tanned leather under different heating methods.

Heating method	AME	VE	BE
Before heating	84.0	74.8	79.1
MIH	93.5	90.4	86.2
WBH	90.8	84.8	85.0

3.5 Physical and Mechanical Properties

Table 3. The tear strength of Ti(III)-tannin tanned leather under different heating methods.

Tannin	AME		VE		BE	
Heating method	MIH	WBH	MIH	WBH	MIH	WBH
Tear force /N	39.48	32.81	43.80	35.11	56.41	37.69
Tear strength /$N{\cdot}mm^{-1}$	15.19	14.82	21.87	18.33	19.28	16.87

Tearing force is one of the important physical properties of the leather products. Due to the special woven structure of the leather, the leather not only has high tensile strength but also high tearing force, which is one of the rare and valuable properties of leather. Table 3 records the tear strength of Ti(III)-tannin tanned leather under different heating methods. It is observed that the tear strength of experimental sample is higher than that of control. That was, microwave irradiation might promote synergistic effect between tannin and Ti(III), thereby, the effective connection between the collagen fibres was enhanced and the strength of the collagen fiber weaving network was increased.

3.6 SEM Analysis

Fig. 4 shows the SEM image of Ti(III)-tannin tanned leather. It is obvious from the picture that the leather is woven from fibres apparently and the magnification is X 25. When it is further magnified (X 5000), the fibres of the samples are obviously woven from finer fibres. Moreover, there are bright and dark grainy stripes on the fibre bundle of the sample (X 20,000 and X 50,000), which is the performance of a quarter of the split structure of collagen fibres. These results reflected that both of the method (MIH and WBH) did not destroy the hierarchical structure of collagen in the tanned leather. However, microwave could promote the combination of tannins and collagen and make the fibre structure more compact.

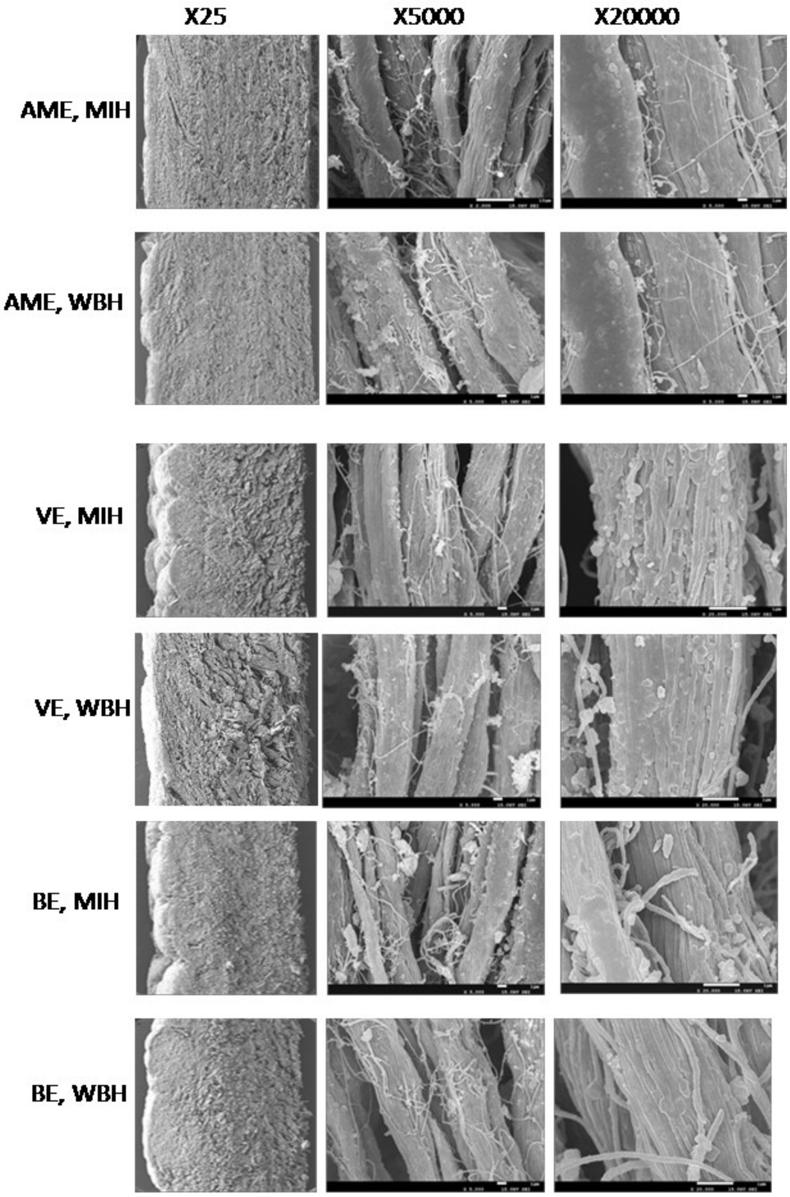

Fig. 4. SEM image of Ti(III)-tannin tanned leather.

4 Conclusion

In this study, the influence of microwave on the complex reaction of Ti(III) with tannin extracts and tanned leather products properties were investigated. The results showed that microwave irradiation can accelerate the complex reaction of Ti(III) with tannin extracts. At pH 3-4 and room temperature, the mixture of tannin and Ti(III) could be used as a combination tanning agent Evidences indicated that microwave could increase the shrinkage temperature, tear strength, and fibrage of Ti(III)-tannin tanned leather, and it would not change the combination mode of the skins with tanning agents as well as the hierarchical structure of collagen. Hence, microwave may have an ability to promote the reaction between Ti(III) and tannins and the combination of tannins with collagen, providing a theoretical basis for the application of microwave in Ti(III)-tannin combination tanning technology.

Acknowledgement

The authors wish to thank the National Natural Science Foundation of China (No. 21576171) for financial support.

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