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Aluminum tanning of hide powder and skin pieces under microwave irradiation

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Abstract

The application and mechanism study of microwave irradiation in traditional industries have attracted considerable attention owing to the unique thermal and athermal effects that could lead to unexpected benefits in high-efficiency and clean production. Herein, we report the investigation of the aluminum tanning under microwave irradiation upon using hide powder and skin pieces, respectively, as simulants of real hide or skin. The aluminum tanning process and the tanned products under microwave heating (MWH) were studied and compared with those of conventional water bath heating (WBH) as the controls. For the tanning system of hide powder, the tanning effluents were analyzed in terms of pH, conductivity, dielectric constant and aluminum content, and the tanned powder was investigated by differential scanning calorimetry (DSC), thermogravimetric (TG) analysis, and FT-IR spectroscopy. For the skin piece system, the pH and aluminum content of tanning effluents were also determined, and at the same time, DSC, TG, SEM, FT-IR and shrinkage temperature were used to illustrate the actions of microwaves on the structure and properties of the tanned pieces. The results show that aluminum reactivity in the penetration and binding process of collagen fibers in hide powder and skin pieces improved using microwave treatment. The residual aluminum content was greatly reduced by microwave heating action, and the increased amount of aluminum with even distribution was observed in the tanned products. Microwave irradiation also resulted in the tanned products with better thermal stability and thermal decomposition resistance. This work further promotes application of microwave treatments for aluminum-based tanning in leather industry.

Keywords: Microwave, Aluminum tanning, Hide powder, Skin pieces, Thermal effect, Non-thermal effect

1 Introduction

Tanning is regarded as the most crucial process for converting raw hide (or skin) into leather through cross-linking reactions between the reactive groups of collagen fibers and tanning agents, and this process improves the thermal and structural stability of hide collagen matrix [1]. Notably, the tanning process is a complex chemical reaction process that is often carried out upon heating. Thus, it is possible to apply microwave irradiation during the tanning period as a heating source. Microwave is an electromagnetic wave showing a frequency range of 300–300,

000 MHz [2]. It has various advantages such as energy saving, even heating and accelerating reaction rate because of its unique physical, chemical and biological effects [3–10], and it has been widely used in many fields of industry, agriculture, military and communication [11]. Microwave irradiation presents not only thermal effect to increase the temperature of the tanning system, but also a non-thermal effect that is favorable for application to chrome tanning [12–17], vegetable tanning [18, 19], zirconium tanning [20], titanium tanning [21] and aldehyde tanning [22–25]. For example, Costa et al. [17] found that the reaction between Cr (III) and ethylenediaminetetraacetic acid was accelerated upon introduction of microwaves to form purple complexes. Chen et al. [13, 14] investigated the action of microwave irradiation on the stability of Cr (III) complexes using UV-visible spectrophotometry. It was found that carboxyl-containing ligands reacted with the nitrate

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and sulfate groups of Cr (III) salts to produce different types of Cr (III) complex products. They found that, under microwaves, the reaction rate and chelate stability of Cr (III) complexes were greatly improved, indicating that microwaves promote multinuclear coordination of Cr (III) and hide collagen fibers. Furthermore, Wu et al. [18] studied the binding properties of tannin extract with collagen fibers using microwave as heating sources. The thermal stability of leather was improved under microwave irradiation. Compared to heating using a water bath, the shrinking temperature was increased by about 1 °C, and the content of macromolecular tannin and phenol components in the tanning liquid was decreased. The investigations of these authors confirm that microwave heating promotes the penetration of plant tannins into the skin and the binding to collagen fibers.

Aluminum tanning is also an important tanning method, and it has been used to develop chrome-free tanning systems. Its operation is similar to chrome tanning [26], and the development of new aluminum tanning agents and aluminum-based tanning methods has attracted considerable attention [27, 28]. At present, the main methods of modification of aluminum tanning are developing new coordination groups [29–32] and combination with other tanning methods [33–36]. Notably, microwave irradiation was also investigated for its application in the aluminum tanning process owing to its unique thermal and athermal effects [37, 38]. In our previous work, the microwave-heated hydrolysis and olation behavior of aluminum sulfate [37] and their crosslinking reactions with collagen [38] were studied in the homogeneous system. These investigations confirm the great advantage and potential of microwave heating in aluminum tanning, but the actual aluminum tanning process that is carried out in the heterogeneous system has not yet been covered. Actual aluminum tanning is a material-exchange reaction between aluminum complexes in solution and solid hides, and the tanning process also involves penetrating and binding actions of aluminum tanning agent in the collagen fiber matrix [1]. Therefore, in this paper, the use of hide powder and skin pieces is presented as a research goal to simulate actual aluminum tanning. Hide powder is a flocculent powder obtained from a series of processes such as liming, deliming, demineralizing, buffering, dewatering and pulverizing using raw hide as the starting material [39]. Because the fiber is relatively homogeneous and there is no difference in position, hide powder is often used as a standard reagent for the analysis of tannin content in tannin [40]. However, there is no complex spatial weaving structure of collagen fibers in hide powder. The bundles are in a separated state and cannot accurately reflect the penetration and binding process of aluminum to collagen fibers. Thus, skin pieces were further used to deeply investigate the action of microwave on aluminum

tanning. Overall, in the present work, microwave heating (MWH) was applied to the aluminum tanning of hide powder and skin pieces, and the corresponding tanning experiments under water bath heating (WBH) were regarded as controls, as shown in Scheme 1. For the tanning system of hide powder, the tanning effluents were analyzed in terms of pH, conductivity, dielectric constant and aluminum content, and the obtained tanned powder was analyzed by differential scanning calorimetry (DSC), thermogravimetric (TG) analysis, and FT-IR methods. For the skin piece system, the pH and aluminum content of tanning effluents were also determined, and at the same time, DSC, TG, SEM, FT-IR and shrinkage temperature (T_s) were used to illustrate the action of microwave on the structure and properties of tanned pieces. These analysis methods present a great benefit to provide information on aluminum tanning towards cleaning production and better leather performance with microwaves.

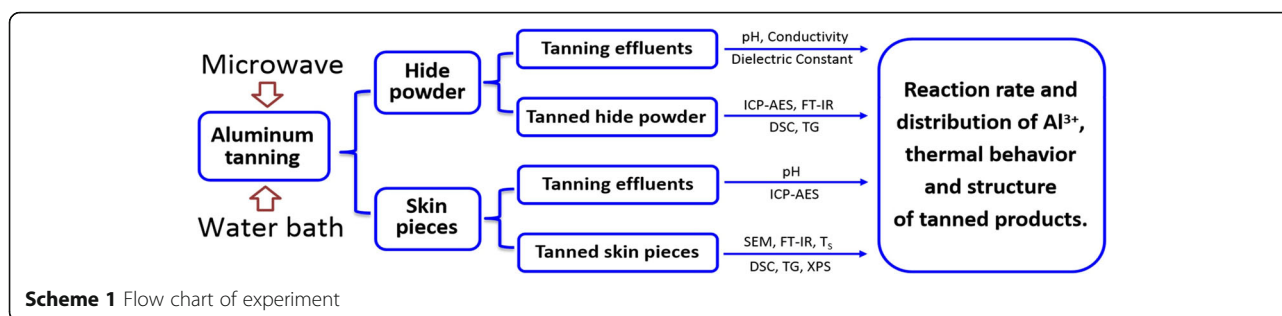
2 Experimental

2.1 Materials

White hide powder was provided by the Institute of Chemical Industry of Forest Products, Academy of Forestry, China. Pickled goatskin with average area of 4–5 square meters was used for the tanning processing. $Al_2(SO_4)_3 \cdot 18H_2O$ was purchased from the Aladdin Reagent Company (Shanghai, China). All the other chemicals used were analytical reagent, commercially purchased and used without further treatment.

2.2 Aluminum tanning of hide powder

Seventy grams of NaCl was dissolved in 1000 mL of distilled water to prepare the NaCl solution (70 g/L) as the solvent for the tanning agent. The aluminum tanning agent was prepared by dissolving 3.265 g of $Al_2(SO_4)_3 \cdot 18H_2O$ in 50 mL of the above NaCl solvent, and its pH was determined to be 2.20. $NaHCO_3$ (1.2346 g) was added to the above solvent (molar ratio of Al^{3+} to HCO_3^- : 1:1.5). White hide powder (5.0 g) and the above NaCl solution (50 mL) were added in a conical flask (250 mL), and the obtained mixture was shaken vigorously for 30 min at room temperature (RT) at about 25 °C. Then, 50 mL of aluminum tanning agent was added to tan the hide powder. The microwave samples were placed in a microwave reactor (Xian Yuhui MCR-3 microwave chemical reactor, China), while the controls were heated in a water bath shaker. Aluminum tanning was conducted for 30 min at 30, 40 and 50 °C, respectively. All the tanning systems were then basified by slowly adding 20 mL of $NaHCO_3$ solution (61.73 g/L). After that, all the microwave and control samples were further treated for 30 min at 30, 40 and 50 °C, respectively. The tanning effluent was collected by filtration for further analysis, and the tanned hide powder was obtained and dried in a freeze dryer.



2.3 Aluminum tanning of goatskin pieces

The NaCl solution (100 g/L) was prepared and used as solvent for the tanning agent. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (194.7 g) was dissolved in the NaCl solution (1.0 L) to prepare the aluminum tanning agent with the concentration of 100 g/L. Skin pieces (2 cm × 6 cm) were prepared by symmetrically cutting the pickled goatskin along its back line. Each skin piece (50 ± 1 g) was soaked in 500 mL of the aluminum tanning agent in a beaker (1000 mL). The microwave samples were stirred at 40 °C in the microwave reactor, while the controls were placed in a water bath shaker at 40 °C. The total tanning time was 10 h, and the pH values of all the tanning systems were determined every hour. After 5 h, the basifying treatment was conducted by adding 1 g of NaHCO_3 into the beakers. The interval of basifying is 1 h, and this treatment was carried out altogether five times. After 10 h, all the tanning effluents and tanned skin pieces were collected and kept for further analysis.

2.4 Analysis of tanning effluent, tanned hide powder and skin pieces

A PHS-3C pH meter (Shanghai Leici Instrument Factory, China) was adopted to measure the pH values of tanning liquors. A DDS-307 conductivity meter (Shanghai Leici Instrument Factory, China) was used to determine the electrical conductivity of tanning liquor. The dielectric constant was recorded using a dielectric constant meter (DZJC, Nanjing Dasha Mechanical and Electrical Technology Institute, China). The inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 2100, Perkin-Elmer, USA) was applied to determine the aluminum content of tanning effluent and tanned samples. DSC measurements were carried out under N_2 atmosphere on a differential scanning calorimeter (DSC200 PC, Netzsch, Germany). The determined temperature range was 30–200 °C with a heating rate of 10 °C/min. TG analysis was carried out under N_2 atmosphere using a TGA/DSC Mettler Toledo (Switzerland). The determined temperature range was 50–700 °C with a heating rate of 10 °C/min. The shrinkage temperature (T_s) was measured on MSW-YD4 (Shanxi, China). The heating medium was water, and the heating rate was 2–3 °C/min from room

temperature (RT, 25 °C or so). The infrared spectra were measured on a Fourier transform infrared spectrometer (Nicolet iS10, Thermo Scientific, USA) in the range of 400–4000 cm^{-1} . SEM determination was conducted on a scanning electron microscope (JSM-7500F, JEOL, Japan), and the distribution of aluminum element in the samples was scanned at the same time by the coupled energy dispersive X-ray spectroscopy (EDX) detector. The surfaces of cut skin pieces were coated with gold before SEM observations. X-ray photoelectron spectroscopy (XPS) measurements were conducted on SXAM-800 (Kratos, UK) to determine the characteristic signals of C, O, N and Al elements. The conditions for XPS are: radiation source of Al $K\alpha$, energy range of –5–1200 eV, illuminance area of 300 $\mu\text{m} \times 700 \mu\text{m}$, tube voltage of 15 kv and tube current of 10 mA.

3 Results and discussion

3.1 Effect of microwave irradiation on the aluminum tanning of hide powder

3.1.1 Analysis of tanning effluents

During the aluminum tanning process, the hydrolysis and olation of aluminum complexes take place, which leads to the increase of hydrogen ion (H^+) and free charged ions in the tanning system, resulting of uneven charge distribution in the complex molecules [1]. These characteristic changes were characterized by detecting the pH, conductivity, dielectric constant and aluminum content in the aluminum tanning effluent [37]. As shown in Table 1, the pH values of tanning effluents at 30–50 °C under microwave heating (MWH) were measured and compared with those treated by water bath heating (WBH). As expected, with the increase of the reaction temperature, the decreased tendency of pH was observed for both MWH and WBH, which is attributed to the improved hydrolysis and olation of the aluminum complexes. At the same temperature, the MWH system always exhibited lower pH value than the WBH system, and this trend is more and more obvious along with temperature increase. Similarly, compared to the WBH controls, the MWH samples possessed lower conductivities in their effluents, which resulted from the increased absorption of aluminum complexes by hide powder.

Table 1 Analysis for the tanning effluents of hide powder under different heating methods

| | WBH | | | | MWH | | | |
|-------|------|----------------------|---------------------|---------------------------------------|------|----------------------|---------------------|---------------------------------------|
| | pH | Conductivity (mS/cm) | Dielectric constant | Al ₂ O ₃ (mg/L) | pH | Conductivity (mS/cm) | Dielectric constant | Al ₂ O ₃ (mg/L) |
| 30 °C | 4.11 | 35.3 | 1616.77 | 1240.62 | 4.09 | 35.1 | 1622.17 | 1216.44 |
| 40 °C | 4.08 | 42.3 | 1648.75 | 1221.73 | 4.04 | 40.5 | 1738.75 | 1211.91 |
| 50 °C | 3.98 | 57.9 | 1657.86 | 895.33 | 3.87 | 57.4 | 2006.79 | 891.56 |

This point was further confirmed by the results of residual aluminum content in the effluents. Table 1 shows that, at 30, 40 and 50 °C, the measured Al₂O₃ concentrations are 1216.44, 1211.91 and 891.56 mg/L, respectively, in the MWH effluents, whereas for the WBH effluents, the corresponding values are 1240.62, 1221.73 and 895.33 mg/L. Thus, MWH led to the increased absorption values of 24.18 mg/L at 30 °C, 9.82 mg/L at 40 °C and 3.77 mg/L at 50 °C, respectively. Furthermore, for the dielectric constant of tanning effluent, increased data were observed for the MWH systems at all the tested temperatures. Concretely, the dielectric constants for the MWH effluents are 1622.17 at 30 °C, 1738.75 at 40 °C and 2006.79 at 50 °C, respectively, whereas in the WBH spent liquors, the corresponding values are 1616.77, 1648.75 and 1657.86. The increased values by MWH are 5.4 at 30 °C, 90.0 at 40 °C and 348.93 at 50 °C, respectively. Dielectric constant is related to the polarity of the tanning system [6]. Heating could lead to the promoted hydrolysis and olation actions of the aluminum tanning agent, which increased the polarity of the tanning liquor. Herein, the dielectric constant is positively related to the temperature change. The higher dielectric constants of MWH is explained by the improved binding ability of aluminum complexes with hide powder and the resulting increased diversity of components in the residual effluents. In short, the above results indicate that temperature increase by both WBH and MWH accelerates hydrolysis and olation of the aluminum complexes, and thus promotes their absorption and combination by hide powder. MWH shows better ability than WBH in this promotion, however. This is because, under microwaves, charged particles and polar ions are forced to oscillate along with the change of electromagnetic field, and the frequency of intermolecular collisions is further increased [6], which is not only beneficial to hydrolysis and olation in the tanning system, but also promotes the participation of carboxyl groups of collagen in the combination with aluminum ions.

3.1.2 Analysis of tanned hide powder

Figure 1 shows the Al₂O₃ contents of tanned hide powder at different temperatures by both WBH and MWH. Obviously, the aluminum content in tanned hide powder is improved by increasing the tanning temperature, whether through WBH or through MWH. When the

temperature was increased from 30 °C to 40 °C and then 50 °C, the measured Al₂O₃ contents were improved from 47.24 mg/g to 49.21 mg/g and then 52.04 mg/g in the WBH system, whereas in the MWH atmosphere, the corresponding values are 49.62, 51.72 and 54.08 mg/g, respectively. At all the tested temperatures, compared to the conventional WBH, MWH led to higher aluminum contents in the resulting tanned hide powder. This is because microwaves promote the cross-linking process between the aluminum agent with hide collagen [41] and the firmness of the formed cross-linking bonds is better just as microwaves accelerate and promote other chemical reactions.

Thermal stability, which is closely related to the structural stability of tanned products and the configuration of collagen molecules, is reflected by the results of DSC analysis. In the DSC curves, the absorption peak corresponds to the thermal denaturation temperature (T_d) of the collagen-based material [42]. Generally, the more the cross-linking bonds locate among the collagen fibers, the greater T_d of the tanned leather are. As shown in Fig. 2, when the tanning temperature was 30, 40 and 50 °C, respectively, the corresponding T_d values of tanned hide powder treated in the WBH system were 67, 81 and 81 °C; for the samples in the MWH system, the T_d results improved to 77, 83 and 84 °C, respectively. At the same temperature, MWH leads to higher T_d than WBH, which indicates that microwave irradiation possesses the

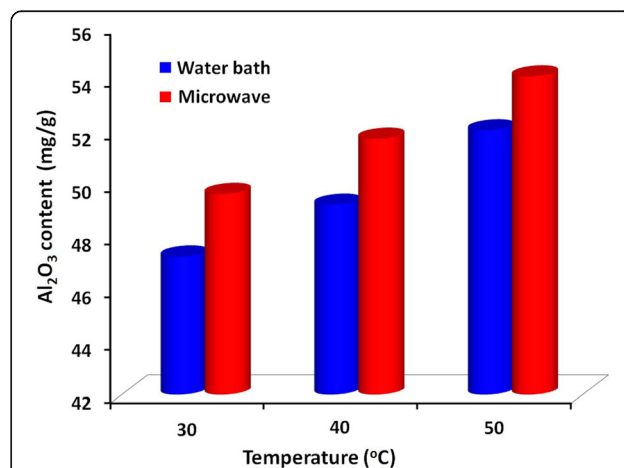


Fig. 1 Aluminum contents of hide powder tanned at 30 °C, 40 °C and 50 °C under different heating methods

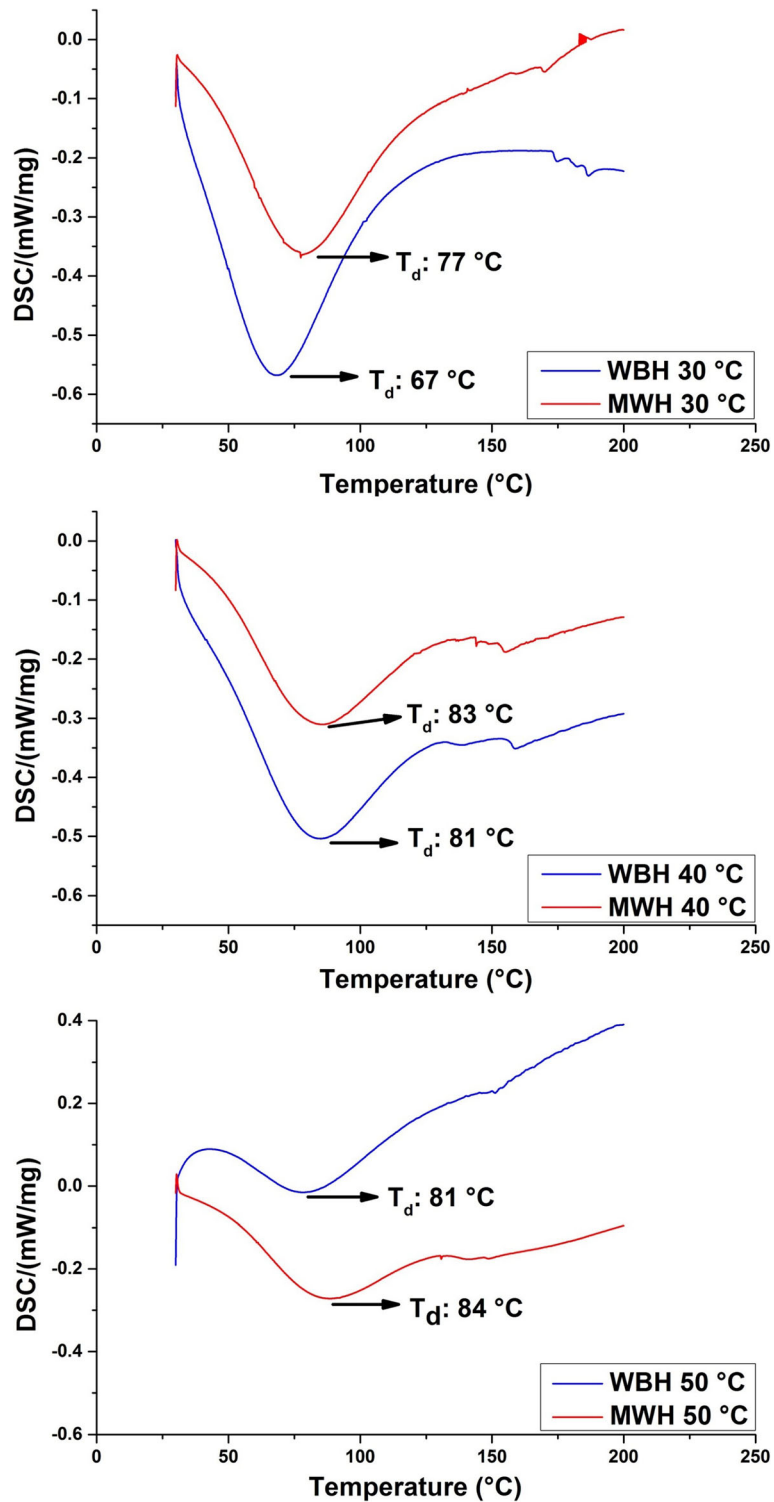


Fig. 2 DSC curves of hide powder tanned at 30 °C, 40 °C and 50 °C under different heating methods

improved ability to promote and further fix the formation of cross-linking bonds between the collagen fibers and aluminum complexes. Thus, the resulting hide powder presents a better thermal stability. When the

aluminum tanning was conducted at 30 °C, a relatively low temperature, the T_d of MWH sample (77 °C) was greatly higher than that of the WBH control (67 °C). The difference between the two samples was about 10 °C.

This great difference is resulted from the athermal effect of microwave irradiation, which is more prominent at lower temperature. When the tanning temperature was improved to 40 or 50 °C, this difference was only about 3 °C, which is explained by the dominance of thermal effect of microwave at higher temperatures.

The TG technique was further adopted to characterize the thermal stability of tanned hide powder. Table 2 shows the maximum thermal decomposition temperature (T_{max}) of the tanned hide powder and the mass-loss ratios at three stages. The corresponding TG and DTG curves are provided in Figs. S1, S2, S3, S4, S5 and S6 in the supplementary information (SI). Like the cases of other collagen-based materials, all the TG curves of tanned hide powder possess three mass-loss stages during the heating range from 50 to 700 °C. The first mass-loss mainly occurred at 40–120 °C, and the corresponding mass-loss ratios were about 13%. This thermal mass-loss is mainly attributed to the removal of H₂O and other volatile substances with small molecular weight in hider powder [41]. Especially, for each TG curve, the weight-loss in the first stage was deduced to calculate the weight-loss data in the second and third stages, which is beneficial to study the thermal stability of tanned hide powder without the impact of water.

The biggest mass-loss process of all the TG curves is the second stage, as a result of collagen decomposition during the pyrolysis process [41]. According to Table 2, the second mass-loss ratios of aluminum tanned hide powder were also moderately different at different tanning temperatures. For example, for the tanning at 30 °C, the mass-loss ratios are 41.1% for MWH and 41.9% for WBH, respectively. When the temperature was increased to 40 °C, the mass-loss ratios decreased to

40.3% for MWH and 41.3% for WBH. When the temperature was further improved to 50 °C, the mass-loss ratios are reduced to 37.6% for MWH and 38.9% for WBH, respectively. These results indicate that, along with the increase of tanning temperature, mass-loss ratio in the second stage reduced gradually. The reason is that the cross-linking degree in hide powder gradually increased. The thermal decomposition resistance was thus enhanced, as well as the conformation stability of the aluminum tanned hide powder. The second mass-loss ratios for MWH samples were always lower than those of WBH controls at the same tanning temperature, which reveals that MWH leads to an increased thermal stability of the aluminum tanned hide powder.

T_{max} in the second stage is affected by the cross-linking degree and strength between tanning agent and collagen [42]. The higher the cross-linking strength and degree are, the higher T_{max} becomes, which means the better thermal stability of the aluminum tanned hide powder. Specifically, when the aluminum tanning of hide powder was carried out at 30 °C, T_{max} of WBH was 301 °C, whereas T_{max} of MWH was 305 °C. The former was about 4 °C lower than the latter. When the tanning temperature was improved to 40 °C, the T_{max} values improved to 306 °C for WBH and 307 °C for MWH, and the difference value between them was 1 °C or so. When the tanning was performed at 50 °C, the T_{max} data were further increased to 308 °C for WBH and 309 °C for MWH, and the difference between the two groups was about 1 °C. As expected, the T_{max} values of MWH samples are always higher than those of WBH controls, which indicates that microwave irradiation exhibits greater promotion for the cross-linking interaction

Table 2 TG analysis of tanned hide powder obtained under different heating methods

| Sample | T_{max} (°C) | Mass-loss ratio of the first stage (%) | Mass-loss ratio of the second stage (%) | Mass-loss ratio of the third stage (%) | Residue ratio (%) |
|--------|----------------|--|---|--|-------------------------|
| 30 °C | | | | | |
| WBH | 301 | 12.4 | 36.7/41.9 ^a | 3.20/3.7 ^a | 47.72/54.5 ^a |
| MWH | 305 | 12.1 | 36.1/41.1 ^a | 3.10/3.5 ^a | 48.66/55.4 ^a |
| 40 °C | | | | | |
| WBH | 306 | 13.6 | 35.7/41.3 ^a | 2.25/2.6 ^a | 48.52/56.1 ^a |
| MWH | 307 | 13.5 | 34.9/40.3 ^a | 3.15/3.6 ^a | 48.36/55.9 ^a |
| 50 °C | | | | | |
| WBH | 308 | 13.4 | 33.7/38.9 ^a | 3.34/3.9 ^a | 49.54/57.2 ^a |
| MWH | 309 | 13.0 | 32.7/37.6 ^a | 3.20/3.7 ^a | 51.08/58.7 ^a |

^aThe value calculated when the moisture content is deducted

between aluminum complexes and collagen fibers, and the tanned products thus have better thermal decomposition resistance. In addition, when the tanning temperature was performed at a lower temperature of 30 °C, the T_{\max} difference between MWH and WBH was the largest. This shows that the non-thermal effect of microwave is more prominent at lower temperature, corresponding to the results of DSC.

As can be seen from Table 2, a slight weight-loss took place in the third stage, resulting from further decomposition of organic molecules in hide powders. There is no great difference among WBH and MWH samples, although the former normally exhibit slightly larger values than the latter. The residue ratios were 54.5% of 30 °C, 56.1% of 40 °C and 57.2% of 50 °C, respectively, for the WBH controls, whereas for the MWH samples the corresponding ratios were 55.4%, 55.9% and 58.7%, respectively. The residue is composed of the carbonization products of aluminum tanned hide powder. Normally, the MWH samples show higher residue ratios than WBH controls under the same conditions, which is attributed to the firmer combination of aluminum tanning agent with hide fibers due to the thermal and athermal effect of the microwaves [38].

The IR spectra of aluminum tanned hide powder with different heating methods are shown in Fig. S7 of the SI. No large difference was observed by comparing the IR spectra of WBH and MWH samples, and the major characteristic peaks of collagen are assigned as follows. The peak at 3414 cm^{-1} corresponds to the amide A band that is resulted from the N–H stretching vibration of the amide groups of collagen macromolecules. The weak absorption peak at 2969 cm^{-1} arises from the amide B band that is related to the C–N stretching vibration. The amide I band, caused by the C=O stretching vibration, is located at 1658 cm^{-1} . The absorption peak at 1550 cm^{-1} is assigned to the amide II band that reflects the N–H stretching vibration intensively coupled to the C–N stretching vibration. The amide III band from the N–H bending vibration is located at 1369 cm^{-1} [43]. The fact that these characteristic bands have no significant change shows that neither MWH nor WBH could lead to the change of collagen structure in hide powder. Even so, the amide A band for the MWH samples was significantly wider than that of the WBH controls. The reason might be that there are association interactions between the N-H and hydrogen bonds leading to the increased number of hydrogen bonds among collagen molecular chains, and further resulting in the decrease in the bond force constant of the N-H bonds and their stretching vibration frequency [44]. This means that, under microwave, there were more functional groups in

collagen molecules of hide powder participating in coordination and binding with aluminum ions.

3.2 Effect of microwave irradiation on the aluminum tanning of skin pieces

3.2.1 pH change during tanning process

The penetration of tanning molecules into hide interior and their binding to collagen fibers are two main processes during aluminum tanning process. Generally, aluminum complexes are supposed to penetrate into hide collagen fibers quickly and uniformly in the early stage of tanning. At a later period of tanning, the environmental pH improved upon basification, and the tanning molecules become larger due to hydrolysis ($[\text{Al}(\text{H}_2\text{O})_6]^{3+} \rightarrow [\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+} + \text{H}^+$) and olation reactions of Al(III) ions. At the same time, the side-chain active groups (e.g. -COOH) of collagen fibers access the inner boundary of aluminum complexes and coordinate with the central Al(III) ion [1]. To further simulate the aluminum tanning process, skin pieces with small size were adopted and tanned under MWH and WBH conditions, respectively. Similarly, the tanning liquors and the tanned leather pieces were analyzed and compared to reveal the effect of microwave irradiation.

Figure 3 provides the pH change of the tanning solution with different heating methods. Whether in the MWH system or in the WBH control, it was clear that pH has decreased gradually during the first 5 h (Fig. 3a). The basification was carried out during the subsequent 5 h by adding some NaHCO_3 every hour, and during this period, the pH of the tanning solution gradually improved to finally reach about 3.8 (Fig. 3b). According to previous works [12] and experimental results of hide powder in the present study, microwave facilitated both the hydrolysis and olation actions in the aluminum tanning process. Thus as anticipated, the pH values of the tanning solution under microwave were always lower than the ones of water bath during the whole tanning period. The reason is relevant to the promotion effect of the microwaves, and also to the higher dielectric constant of the MWH system [12]. The solvent with a high dielectric constant absorbs microwave energy at a significantly increased rate [9]. This increases the probability of collisions among tanning molecules, and in turn accelerates the dissociation rate of side-chain carboxyl groups of collagen fibers and further facilitates their binding with aluminum complexes.

3.2.2 Al_2O_3 content and T_s

Table 3 provides the T_s results of tanned skin pieces, Al_2O_3 contents in tanning effluents and tanned skin pieces under both heating methods. Compared to the case of WBH control, the Al_2O_3 content of tanning effluent in the MWH system was significantly reduced

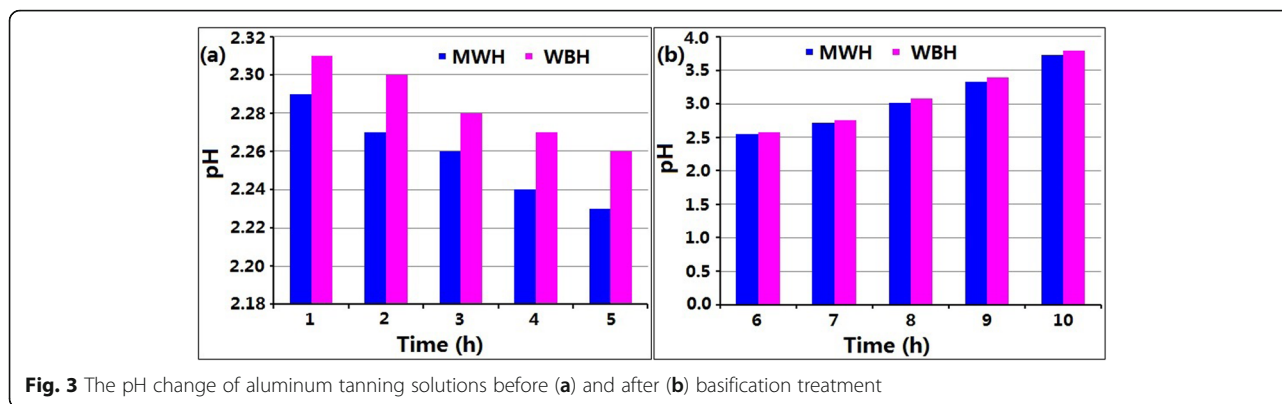


Fig. 3 The pH change of aluminum tanning solutions before (a) and after (b) basification treatment

from 1240.64 mg/L to 895.33 mg/L. Accordingly, the MWH tanned skin piece has significantly higher Al₂O₃ content than the WBH control. The determined values are 38.21 mg/g for the former and 35.74 mg/g for the latter. Thus, these data reveal that the microwaves promote the exhaustion of aluminum tanning agent by skin pieces, thereby significantly reduce the aluminum content in the residual effluent. This is of great benefit for the clean production of aluminum tanning. In addition, Table 3 shows that the T_s of tanned skin pieces under microwave is 74.0 °C, whereas the control provides T_s of only 72.9 °C. Namely, microwave irradiation leads to the increase of T_s by 1.1 °C. This is due to microwave increase of the absorption rate of the aluminum tanning agent during the tanning process; it promotes and further fixes the cross-linking between aluminum tanning complexes and collagen fibers.

3.2.3 Thermal analysis

Similarly, DSC and TG measurements were carried out to study the action of microwave irradiation on the thermal stability of aluminum-tanned leather pieces. Figure 4 shows that the T_d of tanned skin piece heated by

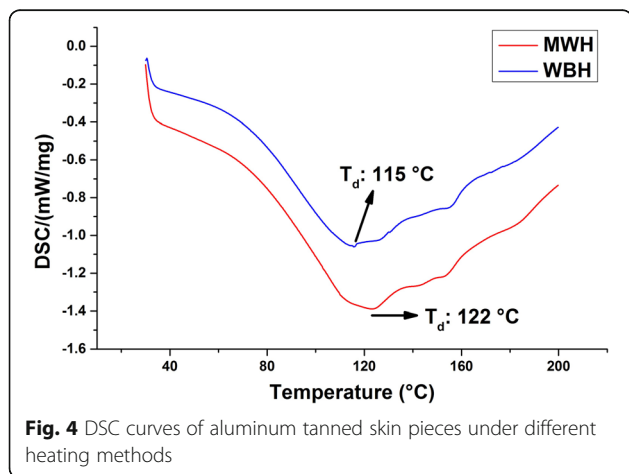


Fig. 4 DSC curves of aluminum tanned skin pieces under different heating methods

microwave is 122 °C, whereas the T_d of the control prepared in water bath is only 115 °C. The former is 7 °C higher than the latter, which further proves the promotion of microwaves on aluminum tanning. Namely, microwave irradiation leads to increased cross-linking combination between collagen fibers and aluminum complexes, and the firmness of cross-linking bonds is improved, too [38]. Thus, the higher thermal stability of the tanned product is observed in the microwave heating system.

Figure 5 shows the TG/DTG curves of aluminum tanned skin pieces with different heating methods. Similar to the case of skin powder (Table 2), the TG curve also presents three distinct weight-loss stages. The first weight-loss mainly occurs at 50–120 °C, too, and the corresponding mass-loss ratios are 21.8% for the MWH sample and 19.1% for the WBH control, respectively. This mainly results from the removal of H₂O and other volatile small-size substances in tanned skin pieces [45]. The obvious weight-loss process on the TG curves is the second stage from 200 to 500 °C, which mainly resulted from the break of cross-linking bonds between collagen fibers [41]. When the content of H₂O is deducted, the revised weight-loss ratios for the second stage are 45.4% for the MWH sample and 46.6% for the WBH control, respectively. As expected, the microwave irradiation results in a deceased value, which is due to the more stable network of tanned skin formed by the increased cross-linking bonds. In addition, the T_{max} values are 317 °C for the tanned skin piece heated water bath and 321 °C for the MWH sample, respectively. Compared to the WBH, MWH leads to the increase of T_{max} by 4 °C. These data also confirm that under microwaves, the degree of cross-

Table 3 T_s and Al₂O₃ contents in tanning effluent and tanned skin pieces

| Sample | Tanning effluent (mg/L) | leather pieces (mg/g) | T _s (°C) |
|--------|-------------------------|-----------------------|---------------------|
| WBH | 1240.62 | 35.74 | 72.9 |
| MWH | 895.33 | 38.21 | 74.0 |

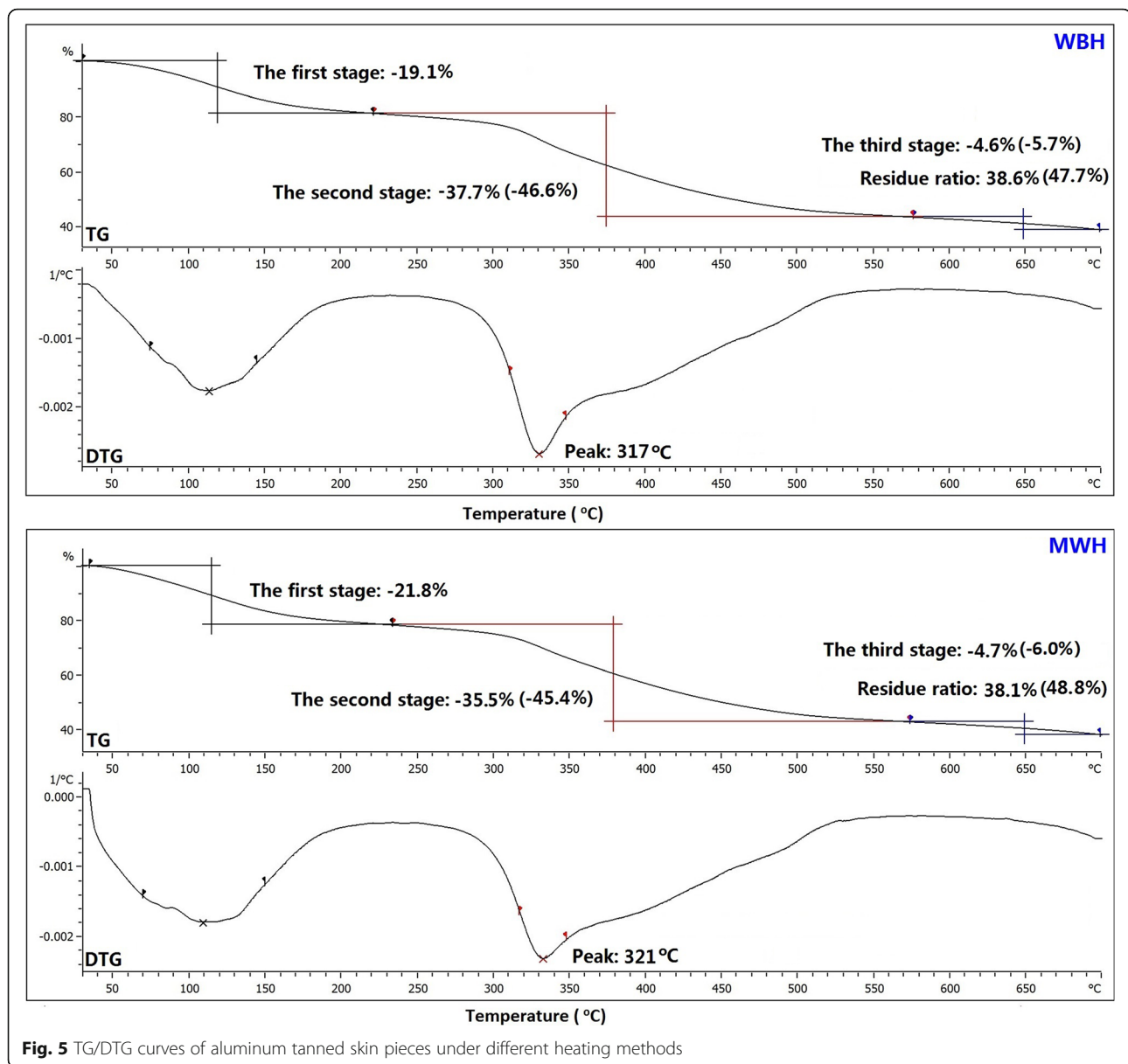


Fig. 5 TG/DTG curves of aluminum tanned skin pieces under different heating methods

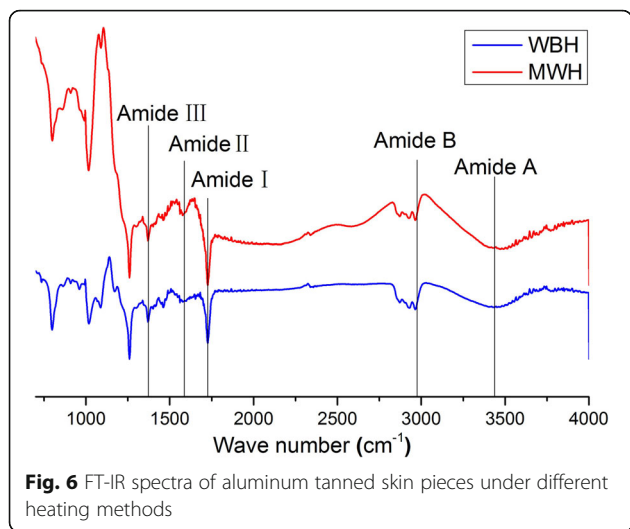
linking between aluminum tanning agent and collagen fibers improves, and the conformational stability of tanned skin pieces is enhanced. This results in an improved thermal decomposition resistance. The third weight-loss stages were also observed for both samples. Like the case of tanned hide powder (Table 2), the tanned skin pieces exhibit slight weight-loss in this stage; no large difference was found for both WBH and MWH samples. The final residue ratios were calculated to be 47.7% for the WBH control and 48.8% for the MWH sample. The increased value for the latter is also a proof for the better thermal stability of tanned skin piece heated by microwaves.

Furthermore, the FT-IR technique was also used to provide the information about the characteristic functional

groups of collagen in tanned skin pieces. These spectra are shown in Fig. 6. The characteristic amide A (3438 cm^{-1}), B (2974 cm^{-1}), I (1726 cm^{-1}), II (1586 cm^{-1}) and III (1369 cm^{-1}) bands are observed in both IR spectra of WBH and MWH samples, and no large difference is found in the position and shape of these peaks, indicating that microwave and water bath do not change the collagen structure of the aluminum tanned skin pieces.

3.2.4 SEM-EDX analysis

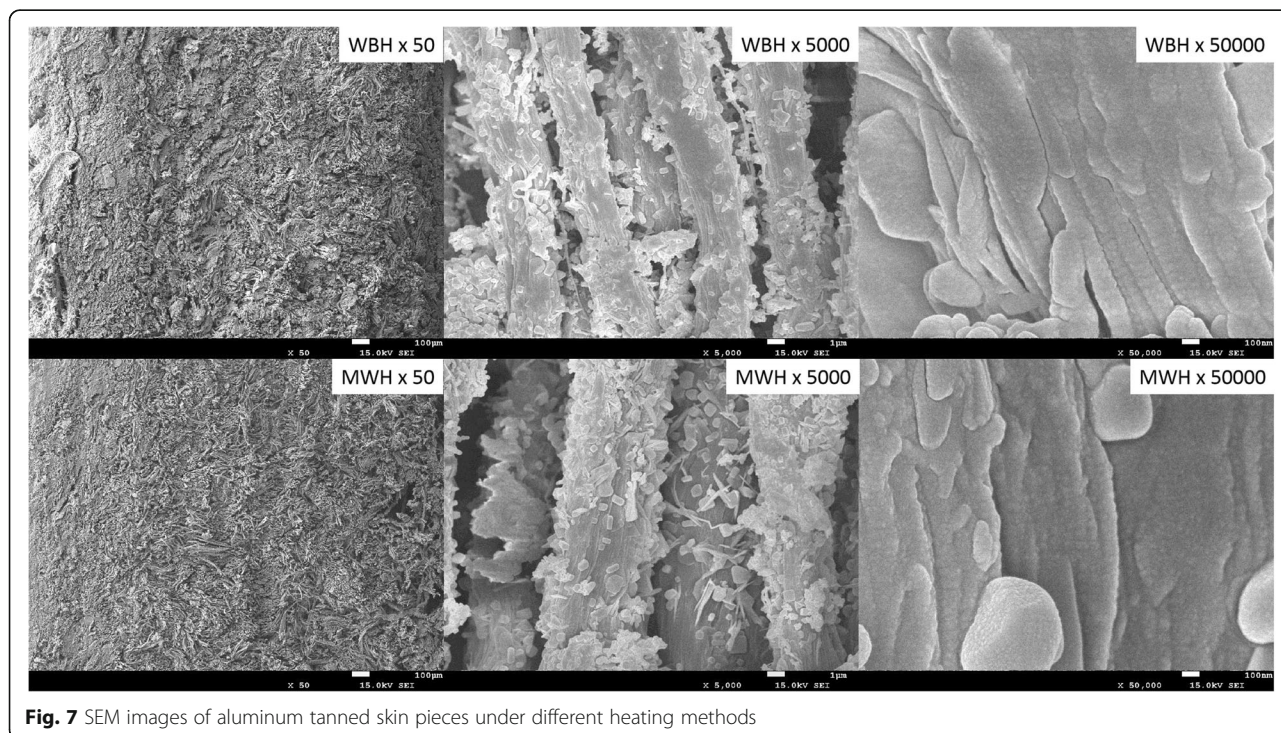
To further explore the action of microwave on the hierarchical structure of aluminum-tanned skin pieces, SEM-EDX analysis was carried out, and the results are illustrated in Figs. 7 and 8. Figure 7 provides the SEM images of aluminum tanned skin pieces with different



heating methods, and the magnifications are 50, 5000, and 50,000, respectively. At the magnification of 50, there is no significant difference on the microstructure between the MWH and WBH samples. When the magnification is improved to 5000, the fiber bundle width of the WBH control is $3 \pm 1 \mu\text{m}$, whereas the width for the MWH sample is increased to $4 \pm 1 \mu\text{m}$, and it's obvious that the collagen fibers under microwave irradiation are tighter. The reason may be that the penetration process of aluminum ions is promoted by microwave irradiation, and thus there are more cross-linking bonds formed in the network of fiber bundles to make the width increase. In addition,

crystal-like particles were found absorbed among or on the fiber bundles, and these particles should be composed of aluminum complexes and other salts. When the magnification is further improved to 50,000, the unique collagen 1/4 staggered structure is shown by the hollow area and the overlapping area [26] in both samples. These results indicate that both MWH and WBH cannot damage the 1/4 staggered structure of collagen fibers.

The distribution of aluminum elements on the cross-sections of tanned skin pieces was also studied by the coupled EDX analysis of SEM measurement, and the corresponding EDX spectra are shown in Fig. 8 and the original SEM images used could be found in Figs. S8 and S9 in the SI. The red signals correspond to the presence of aluminum elements, and their density and distribution are attributed to the content and penetration of aluminum tanning agent on the cross-section of tanned leather. Compared with the WBH control, the signals of the MWH sample are much brighter, and more uniformly distributed in the cross-section of tanned skin pieces. The brighter signals indicate the higher content of aluminum element, which is in line with the above result of Al_2O_3 analysis (Table 3). More importantly, the EDX results confirm the evener distribution of aluminum tanning agent in the cross-section of tanned leather heated by microwave irradiation. This reveals that microwave irradiation not only retains the collagen structure of skin pieces, but also promotes the penetration of the aluminum tanning agent in skin pieces, which is favorable to the improvement of the overall properties of the obtained leather.



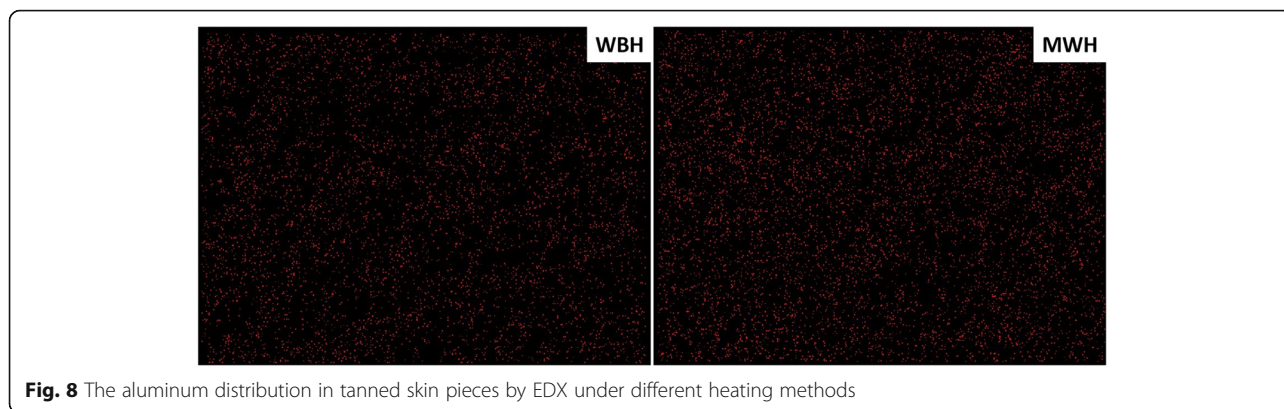


Fig. 8 The aluminum distribution in tanned skin pieces by EDX under different heating methods

XPS measurement is also performed to analyze the action of microwaves on the structure of tanned skin pieces. Figure 9 is the full spectra of XPS including C, O, N and Al elements in a specific orbital binding energy. Figs. S10, S11 and S12 in the SI are the corresponding enlarged spectra of Al, C and O elements. As can be seen from the above XPS spectra, the binding energy of C, O, N and Al in aluminum tanned skin pieces obtained by WBH and MWH did not change significantly. Furthermore, the different peaks at 500 eV and 1100 eV are corresponding to the Na KLL, Na 1s, respectively. The Na element was resulted from the pickling solution containing NaCl used to prevent the acid-swelling of skin

pieces. The XPS results indicate that both WBH and MWH neither change the combination mode of the aluminum tanning agent molecules with collagen fibers in the skin pieces, nor damage the structure of the collagen fibers. Furthermore, the relative signal intensities of Al to C, N and O elements, respectively, in the MWH sample is stronger than those in the WBH control, which is explained by the higher Al content in the tanned skin piece heated by microwaves.

4 Conclusions

In summary, the heterogeneous aluminum tanning of hide powder and skin pieces has been investigated under microwave irradiation. The conventional water bath heating was adopted as the control to study the action of microwave heating on the aluminum-tanning process, and the structure and property of the corresponding tanned products. Both thermal and athermal effects of microwaves were found to be beneficial to the aluminum tanning, and the following main conclusions could be drawn:

- (1) Microwave heating promoted the absorption, penetration and bonding process of the aluminum tanning agent, significantly reducing the aluminum content in waste liquid, which is favorable for clean tanning and improvement of the aluminum content in tanned leather.
- (2) Microwave heating presents better thermal stability and thermal decomposition resistance for hide powder and skin pieces.
- (3) The structure of tanned hide powder and skin pieces is not damaged under microwaves.
- (4) This study is of interest for the theoretical guidance and practical reference concerning application of microwaves in aluminum-based tanning. And future work will focused on the development of specialized microwave-heating tanning device (e.g. drum) and the cost estimation, which is beneficial for the large-scale application of this procedure.

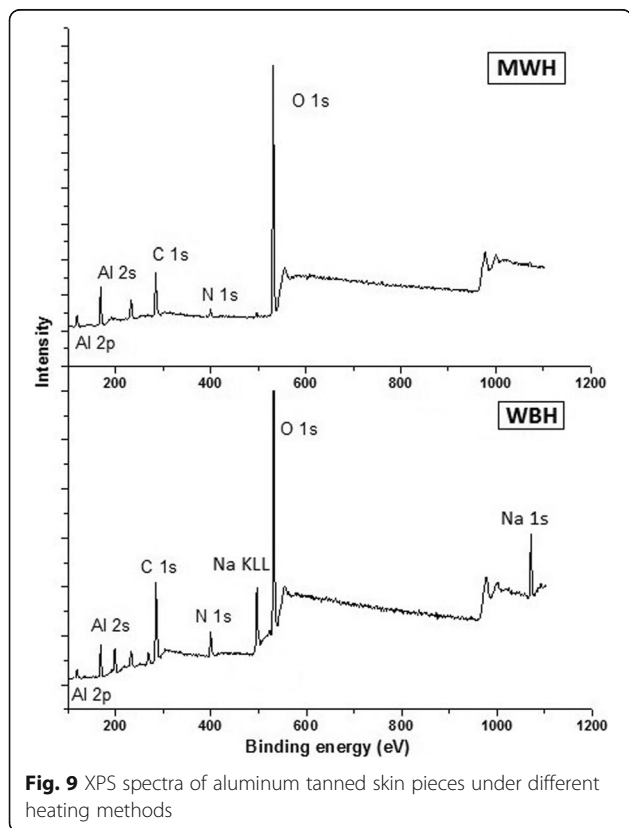


Fig. 9 XPS spectra of aluminum tanned skin pieces under different heating methods

5 Supplementary information

Supplementary information accompanies this paper at <https://doi.org/10.1186/s42825-020-00037-w>.

Additional file 1: Fig. S1. TG/DTG curves of tanned hide powder with WBH at 30 °C. **Fig. S2.** TG/DTG curves of tanned hide powder with MWH at 30 °C. **Fig. S3.** TG/DTG curves of tanned hide powder with WBH at 40 °C. **Fig. S4.** TG/DTG curves of tanned hide powder with MWH at 40 °C. **Fig. S5.** TG/DTG curves of tanned hide powder with WBH at 50 °C. **Fig. S6.** TG/DTG curves of tanned hide powder with MWH at 50 °C. **Fig. S7.** FT-IR spectra of aluminum tanned hide powder at 30 °C, 40 °C and 50 °C with different heating methods. **Fig. S8.** SEM image for EDX analysis for the cross-section of aluminum tanned skin pieces of WBH. **Fig. S9.** SEM image for EDX analysis for the cross-section of aluminum tanned skin pieces of MWH. **Fig. S10.** XPS-Al images of tanned skin pieces with different heating methods. **Fig. S11.** XPS-C images of tanned skin pieces with different heating methods. **Fig. S12.** XPS-O images of tanned skin pieces with different heating methods.

Abbreviations

DSC: Differential scanning calorimetry; EDX: Energy dispersive X-ray spectroscopy; FT-IR: Fourier transform infrared spectroscopy; ICP-AES: Inductively coupled plasma atomic emission spectrometry; MWH: Microwave heating; SEM: Scanning electron microscope; SI: Supplementary information; T_d : Increased thermal denaturation temperature; T_{max} : Maximum thermal decomposition temperature; T_s : Shrinkage temperature; TG: Thermogravimetric; WBH: Water bath heating; XPS: X-ray photoelectron spectroscopy

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Authors' contributions

Yue Liu performed all the experiments and was a major contributor in data analyses and writing of this manuscript. Bin Song took part in the experiments about hide powder. Jinwei Zhang and Carmen Gaidau made substantial contributions to the design and implement of the experiments in this work. Haibin Gu is the superior of this work and made great contribution to the conception of the study, the discussion of the results and the revision of the manuscript. All authors have read and approved the final manuscript.

Authors' information

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Availability of data and materials

All data needed to evaluate the conclusions in the paper are present in the paper and the supplementary material.

Competing interests

The authors declare that they have no competing interest.

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