THE INFLUENCE OF MICROWAVE IRRADIATION ON THE COLLOIDAL PROPERTIES OF VEGETABLE TANNIN EXTRACT SOLUTIONS

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Vegetable tannin extract has an important use as a tanning agent in leather industry. The colloidal properties of vegetable tannin extract solutions, as a critical factor, greatly affect vegetable tanning process. In this work, we have investigated the particle size and Zeta potential of Commercial Acacia Mangium extract solutions (CAME) and Commercial valonia extract solutions (CVE) under water bath heating and microwave irradiation. The selected conditions were as follows: time, 15 min, 30 min, 60 min and 120 min; temperature, 30°C, 40°C and 50°C. It was found that the particle size of both CAME and CVE under microwave irradiation decreased while Zeta potential increased compared with water bath heating. Particularly, the extent of the decreased particle size and increased Zeta potential of CVE is bigger than CAME. Furthermore, the feature becomes more and more significant with the rise of temperature. In the vegetable tanning process, tannin extracts with small particle size can easily penetrate into the skin and then crosslink well with the collagen of skin. Therefore, as a novel, environmentally friendly and efficient thermal method, microwave irradiation may be used for the well-performance leather, less pollution and cleaner tanning process.

Keywords: dynamic light scattering, microwave irradiation, vegetable tannin extract

INTRODUCTION

Microwave is a kind of electromagnetic wave in the frequency from 300 MHz - 300 GHz. It can inspire molecular rotational level transition, thus directly act on the condensed matter molecules in the reaction system, and then cause dipole steering polarization and interfacial polarization to heat materials (Jin *et al.*, 1999). As a novel, mild, environmentally friendly and efficient thermal technology, microwave is widely used in pharmaceutical chemicals (Meng *et al.*, 2010), food chemicals (Kim *et al.*, 2011), life sciences field (Panagopoulos, 2012) and so on. Furthermore, these applications have already achieved fruitful research results.

Vegetable tannin extracts occupy a very important position in the leather industry, and their solutions and actions are extremely complex whether in physics or chemistry. From the composition point of view, vegetable tannin extracts are a complex mixture of polydisperse colloid contains tannins, non tannins and insolubles. In chemistry, vegetable tannins are classified into two categories: hydrolysable tannin and condensed tannin. Hydrolysable tannin is a compound formed by polyphenol acid and its derivatives, glucose or polyol through the ester bonds, which is easily hydrolyzed to the polyols and phenolic acids. In general, condensed tannin is a kind of oligomers or polymers formed by the condensation of flavanol-3-alcohol which is the structural unit through 4→8 (or 4→6) C—C bond, and it shows a different feature from hydrolysable tannin (Zhang *et al.*, 2012). The structures of hydrolysable tannin and condensed tannin are exhibited in Figure 1. There is a reversible equilibrium between the molecular dispersions and colloidal dispersions, thus this system is often referred to as semicolloid (Chen and Li, 2011). The micelle of vegetable tannin extracts is a structure with double electrical layer, namely, adsorption layer directly connected with colloidal nucleus and diffusion layer outside the adsorption layer where about colloidal nucleus. In the electric field, when tannin molecules move towards the anode, positively charged ions in the adsorption layer move together with colloidal particles, while the positively charged ions in the diffusion layer move out of the colloidal particles. Meanwhile, the formed potential difference between colloidal particles and the dispersion medium is called Zeta potential (Chen *et al.*, 2007). The smaller the colloidal particle size is, the greater the diffusion coefficient is. Then tannin particles diffuse easily with great diffusion coefficient and this is calculated by Brownian motion diffusion coefficient calculation formula as follows by (1) (Zhou, 2002):

$$D = \frac{RT}{6\pi\eta\gamma L} \quad (1)$$

Therefore, in the tanning process, the speed of tannin particles penetration is closely related to the size of tannin particles. Thus, with small tannin particles, tannins more easily penetrate into skin in actual tanning process. The colloid chemical properties of vegetable tannin extracts will undergo some changes under microwave irradiation, hence it will lead to transformation in the tanning process, technology and even tanning mechanism. According to Brownian motion, the particles in the form of colloid can be investigated by using dynamic light scattering and the electrophoresis properties of colloid which dynamically measure Zeta potential and particle size distribution of colloidal particles. These properties for the evaluation of the significance of the penetration ability, filling performance and the degree of combination between vegetable tannin extract solutions and hide fibers are more than the chemical characters of the extract solutions themselves (Thorstensen, 1985). In this work, we have investigated the colloidal properties of vegetable tannin extract solutions by using Zetasizer Nano-ZS series equipment and evaluated the stability of the solutions under microwave irradiation and water bath heating in different time and temperature. Finally, the penetration, filling and bonding performance of the tannin extract solutions were explained by using the variation tendency of particles size distribution and Zeta potential measured in this experiment. Therefore, it may provide the experimental basis for revealing electrochemical change in the vegetable tanning process.

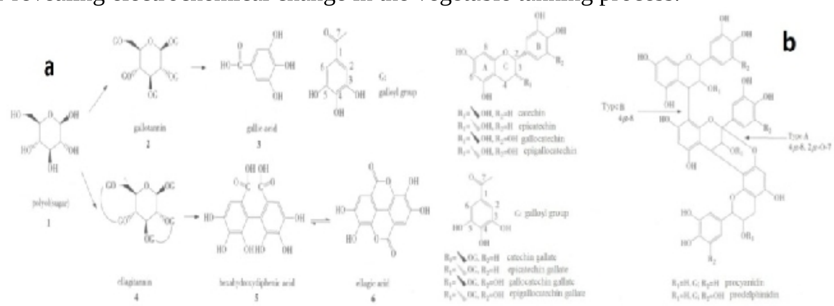

Figure 1. The structure of hydrolysable tannin (a) and condensed tannin (b)

EXPERIMENTAL

Material

Commercial Acacia Mangium extract and Commercial valonia extract were industrial products, commercially purchased from Wu Ming tannin extract factory in Guangxi, China. Microwave irradiation was produced by a Xian Yuhui MCR-3 microwave chemistry reactor. Water bath heating was achieved by a Shanghai

Jihengshiye magnetic stirring water bath pot. Zeta potential and particle size were measured on a Zetasizer Nano-ZS series equipment (Malvern Instruments, UK).

Procedure

Preparation of the original vegetable tannin extract solutions (mass concentration, 4g/L) was achieved according to the literature (Nanjing technological college of forest products, 1980). The gained CAME and CVE solutions were centrifuge at 3000 r/min for 30 minutes. Then, the supernate was collected with clean beaker as a stand-by.

60 mL of CAME and CVE solutions were heated by water bath and microwave irradiation, respectively. The selected conditions were as follows: time, 15 min, 30 min, 60 min and 120 min; temperature, 30°C, 40°C and 50°C. After that, Zeta potential and particle size of the treated tannin extract solutions were measured by Zetasizer Nano-ZS series equipment at the same temperature as mentioned.

RESULTS AND DISCUSSIONS

In leather-making, consideration of oxidation of tannins and denaturation of the collagen caused by a long rotation time under the high temperature, the temperature of vegetable tanning is generally controlled at below 38°C, and 35°C to 38°C is appropriate (Shi and Di, 1998). In order to explore the change law of particle size and Zeta potential of tannin extract solutions in the process of rising temperature, the temperature range for 30-50°C was set up. By the Stokes-Einstein equation, it is known that hydrodynamic diameter of colloidal particles is proportional to the temperature, namely, rise in temperature will increase colloidal particle size. Simultaneously, high temperature can accelerate the Brownian motion of colloidal particles, and more frequent collisions appear among the particles. Thus, there is a substantial reduction in the stability of the solutions (Fu *et al.*, 1990).

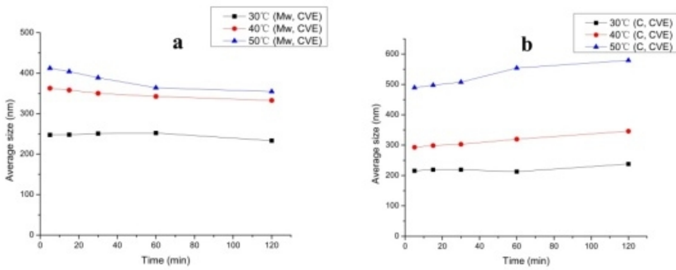

Figure 2. Particle size of CVE under microwave irradiation and water bath heating

The particle size of CVE under microwave irradiation and water bath heating is shown in Figure 2. Under microwave irradiation, the particle size of CVE decreased gradually with irradiation time, moreover, it reduced more significantly when the temperature rose up. As seen in Figure 2b, under water bath heating, the particle size of CVE is smaller within 60 minutes than microwave irradiation. This is because, in the water bath heating process, thermal energy transfer to the external surface of material by convection, conduction and radiation in the existence of the thermal gradient so that the material is heated slowly and unevenly. Nevertheless, in the microwave field, electromagnetic energy directly turns into thermal energy that can generate heat at different depths inside the materials, therefore, the materials are heated more quickly and evenly (Barba *et al.*, 2008). In contrast to Figure 2a and 2b, the particle size of CVE increased with the rising of temperature. But when the treatment is performed for a long time (such as 120 min), compared with water bath heating, the particle size reduced about 70 nm under microwave irradiation. What is more, the reduction was more obvious with the rise of temperature. In a word, the results showed that microwave irradiation may induce the reduction of CVE particle size.

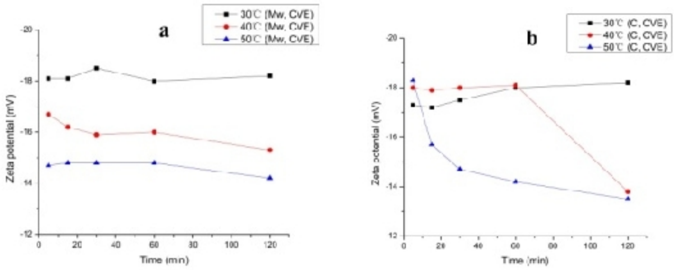

Figure 3. Zeta potential of CVE under microwave irradiation and water bath heating

Zeta potential is an important index value to determine whether the colloidal solution is stable. In general, solution which the absolute value of Zeta potential is more than 30 mV is a stable system, on the contrary, the solution which the absolute value of Zeta potential is within 30 mV is an unstable system (Chen *et al.*, 2007). When Zeta potential value is 0, the solution arrives at the isoelectric point that the solution is most likely to occur micelle aggregation and precipitation phenomenon. So the greater absolute value of Zeta potential indicates more stable vegetable tannin extract solution. Zeta potential of CVE under microwave irradiation and water bath heating is shown in Figure 3. Under microwave irradiation, there was no change in Zeta potential with irradiation time (seen in Figure 3a). However, the absolute value of Zeta potential declined as irradiation temperature increased, and it declined about 3.5 mV from 30°C to 50°C. Nevertheless, under water bath heating, the Zeta potential of CVE showed a falling trend when the heating time increased, and it decreased approximately 4.5 mV while the heating temperature increased from 30°C to 50°C as seen in Figure 3b. Owing to the slowness and unevenness of water bath heating, within 30 minutes, Zeta potential of CVE did not substantially change with the increase of heating temperature, but it showed a regular change under microwave irradiation from the beginning of irradiation. At the same temperature, the absolute value of Zeta potential of CVE irradiated by microwave increased about 1.5 mV compared with water bath heating. From the variation trend point of view, microwave irradiation is better for CVE to maintain a high degree of stability.

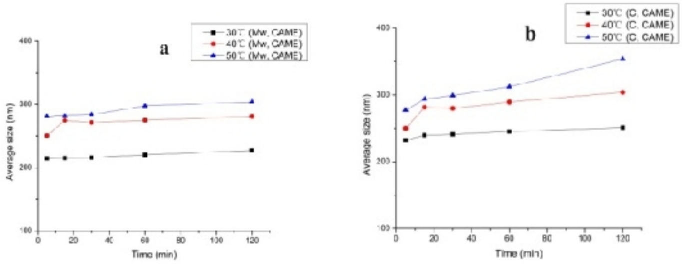

Figure 4. Particle size of CAME under microwave irradiation and water bath heating

The particle size of CAME under microwave irradiation and water bath heating is shown in Figure 4. Under microwave irradiation, the particle size kept essentially unchanged with the irradiation time. However, it increased gradually under water bath heating, and increased more remarkablely when the temperature rose up as shown in Figure 4a. In contrast to Figure 4a and 4b, the particle size increased with the rising temperature, and this is because the hydrodynamic diameter of the colloidal particles is proportional to temperature. Moreover, under microwave irradiation, it increased about 75nm from 30°C to 50°C while increased approximately 95 nm under water bath heating. At the same temperature, the particle size of CAME irradiated by microwave reduced about 30 nm compared with water bath heating. Besides, the higher the temperature was, the particle size reduced more. Therefore, the results showed that microwave irradiation may induce the reduction of CAME particle size.

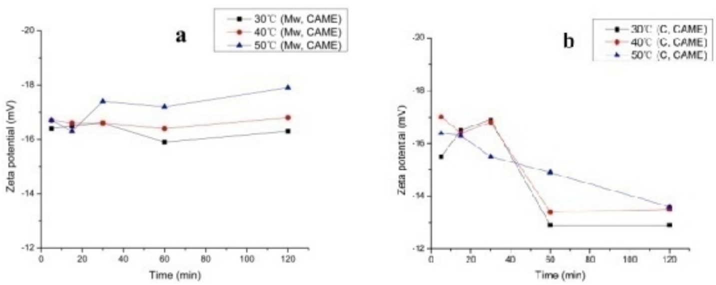

Figure 5. Zeta potential of CAME under microwave irradiation and water bath heating

Zeta potential of CAME under microwave irradiation and water bath heating is shown in Figure 5. Under microwave irradiation, the Zeta potential of CAME remained essentially unchanged with the irradiation time. With the rise of irradiation temperature, the absolute value of Zeta potential increased slightly (about 1.5 mV) from 30°C to 50°C as shown in Figure 5a. The absolute value of Zeta potential of CAME declined 3 mV under water bath heating after 120 minutes treatment (seen in Figure 5b). However, it was obvious that the Zeta potential of CAME remained about the same whatever the different heating temperature was. Under the same temperature, the absolute value of Zeta potential of CAME irradiated by microwave increased about 3.5 mV compared with water bath heating, namely, microwave irradiation might make the properties of CAME more stable.

As seen in Figures 2-5, the particle size of CVE and CAME decreased gradually with the microwave irradiation, and furthermore, it decreased sharply as the temperature rose up. However, the particle size of CVE reduced more under microwave irradiation compared with CAME. As to the Zeta potential, both CVE and CAME kept stable under microwave irradiation. Compared to water bath heating, the absolute value of Zeta potential of both CVE and CAME increased under microwave irradiation, nevertheless, the absolute value of Zeta potential of CVE increased more in comparison to CAME. Since there is some differences in the structures of CVE and CAME (seen in Figure 1), the influence of microwave irradiation on the colloidal properties of CVE is more significant. In microwave electromagnetic field, the polar molecules will produce induced dipole. From the structure point of view, both CVE and CAME are polar molecules with different polarity. Therefore, the effect of microwave irradiation on hydrolysable tannin and condensed tannin is quite different owing to the disparate polarity.

CONCLUSIONS

In this work, we have investigated the influence of microwave irradiation on the colloidal properties of vegetable tannin extract solutions with water bath and microwave heating. And then the colloidal properties were characterized by the particle size and Zeta potential. The results showed as follows: (1) compared with water bath heating, the particle size of CVE (hydrolysable tannin) and CAME (condensed tannin) will decrease as well as the Zeta potential will increase under microwave irradiation. Moreover, the effect is more significant with high irradiation temperature and long irradiation time. (2) Under microwave irradiation, the extent of the decreased particle size and increased Zeta potential of CVE is bigger than CAME. Hence it may be proved that the influence of microwave irradiation on the colloidal properties of hydrolysable tannin is greater than condensed tannin. Notably, as a novel, environmentally friendly and efficient thermal method, microwave irradiation is likely to bring about reduction in the particle size and increase on the absolute value of Zeta potential of tannin extract solutions. Therefore, microwave irradiation may be used for the well-performance leather, less pollution and cleaner tanning process.

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