Particle Size Evolution of Melamain-formaldehyde Tanning Agent on Tanning Effect

by

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Abstract

Melamine-formaldehyde [MF] resin is a tanning agent. Its average particle size [PS] is important for penetrating the skin and thus endowing performance of its resultant leather. The synthesis parameters for MF resin such as pH, molar ratio of formaldehyde to melamine, temperature and reaction time affect its PS. We investigated in detail the growth of MF's PS and its consequent effects on hydrothermal stability, mechanical properties and the apparent properties of leather. The data showed that a broad range of average PS was formed at the different synthesis stages of MF resin. For example, the first reaction stage of methylolation gave an average particle diameter of 250 nm with a narrow size distribution under the conditions of 45°C, 3:1 molar ratio, a pH of 8.5, and a reaction time of 3 hrs. In this case the resultant leather was poor as it had a low shrinkage temperature, lacked fullness and showed a low-valued elongation at break. During the second polycondensation stage, the PS of MF resin increased with increasing reaction temperature and the molar ratio of formaldehyde to melamine. Furthermore, PS increased more rapidly by lowering the pH of the polycondensation and extending its reaction time. Thus, the new average diameter of MF resin particles reached above 3000 nm when the polycondensation reaction was done inside the skin for 2 hours at a pH of 4.5. Consequently, the resultant leather was white and full. It had a high hydrothermal stability and mechanical strength as evidenced by its fully satisfactory elongation at break. Clearly, the cross-links were formed by multiple site interactions between MF resin with large PS and collagen fibers, which enhanced the tanning effect.

Introduction

Tanning involves a process that converts the putrescible hide and skin to resultant leather stabilized against heat, chemical corrosion, mechanical damage and microbiological degradations.[1,2] The prerequisite of tanning is that tanning agent could favorably penetrate into the collagen chains. But the penetration process of tanning agent is influenced by various factors, among which the PS of tanning agent has a great influence on penetration process.[3-5]

For the traditional tannage, the preparation of tanning agent and the tanning process are carried out separately. First, the material with tanning effect is usually prepared in a solid or liquid state, such as chrome tanning agent, titanium tanning agent, amino resin tanning agent, etc.[6] Then, the mechanical action of drum is utilized to force the tanning agent to penetrate into collagen fibers, thus achieving tanning effect.[7] This operation can result in the difficulty of penetration and uneven distribution in the collagen fibers for tanning agent due to inconvenient control of the tanning agent's PS, which reduced the tanning effect. One conventional method of promoting tanning agent's penetration was to strengthen the pre-treatment of the hide by acid, alkali, enzymes and so on to fully disperse collagen fibers.[8] But these treatments made the leather with loose handle and poor mechanical properties.[9]

Another method was to control the PS and structure of tanning agent in tanning process. It has been proved that forming cross-links between tanning agents with small PS and the active groups of collagen fibers was difficult, which resulted in weak tanning effect.[10] On the contrary, the tanning agents with too large size or too complex structure were prevented from penetrating into skin in the early tanning stage, resulting in the leather tanned unevenly with excessive tanning of surface and insufficient tanning of the inner layer.[11] In order to promote the penetration of tanning agent, a series of methods have been taken to control the PS of tanning agent. For example, the masking and changing alkalinity were carried out to control tanning agent's PS for chrome and titanium tannage.[12] The ultrasound technology was employed to decrease the size scale of

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titanium tanning agent.[13] In the vegetable tanning process, a deep sulfurous acid degradation was used to reduce the PS of tannin extract; Similarly, the amino resin tanning agent was subjected to etherification and spray drying, which reduced its self-polycondensation tendency and controlled its PS.[14-16] Although the approaches mentioned above can control the tanning agent's PS to a certain extent, they made the operation cumbersome and reduced tanning effect for weakening tanning agent's reactivity. In recent years, our group has proposed a new tanning method - *in-situ* tannage, that is, the precursor of tanning agent was first allowed to penetrate evenly into bated hides and then it was triggered *in-situ* to produce active tanning agent particles.[17-19] At the first stage, the PS of tanning agent produced *in-situ* was small, and there was no need to consider the problem of penetration; at the second stage, these small particles can be further triggered to become larger. However, how the PS of tanning agent affects the tanning property of resultant leather is still in suspense.

As a continuous work, in this paper, we take the *in-situ* produced melamine-formaldehyde (MF) oligomer as an example, the effect of parameters such as reaction pH, molar ratio of formaldehyde to melamine, reaction temperature and reaction time on tanning agent's PS were investigated. Simultaneously, the impact of PS **evolution** of MF tanning agent on thermal stability, mechanical properties and apparent properties of the resultant leather were measured in detail. We aim at declaring the influence of the tanning agent's PS evolution on tanning effect, thus achieving the predictable tanning property by controlling the PS of tanning agent.

Experimental

Materials

Formaldehyde (37%), melamine, formic acid, hydrochloric acid, sulfuric acid, sodium bicarbonate, sodium carbonate and sodium hydroxide of analytical pure were obtained from Chengdu Kelong Chemical Engineering Co., Ltd. (Chengdu, China). Bated goat skin used in this study was made in our laboratory. Fatliquor was supplied by Chengdu Ruiqi Chemical Co., Ltd. (Chengdu, China).

Reaction of Melamine and Formaldehyde

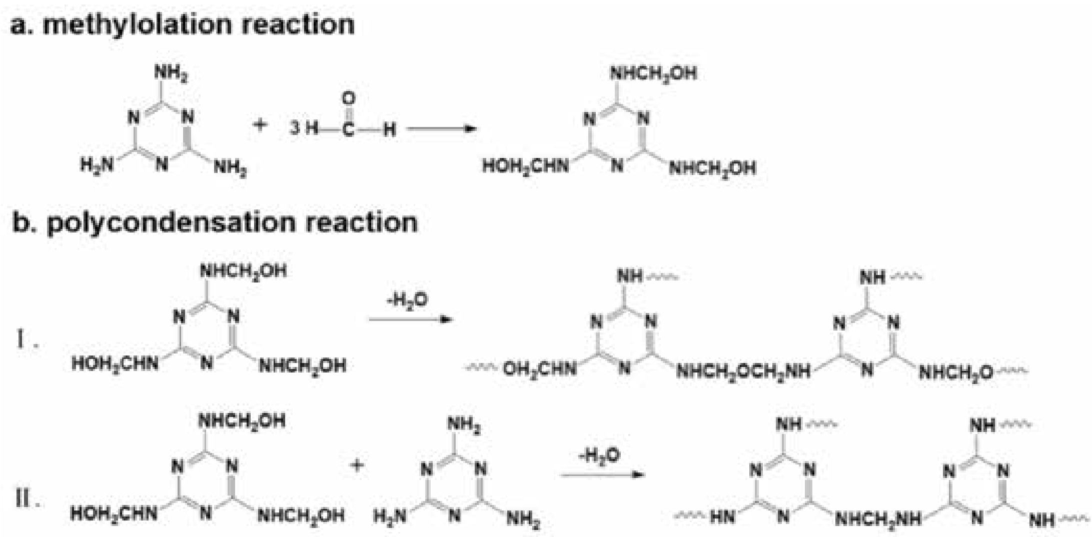
Melamine and formaldehyde reaction diagram was shown in Scheme 1. A certain amount of melamine and deionized water were added to a 250 mL three-necked flask equipped with a thermometer, a stirrer and a reflux condenser. The weighed formaldehyde was added to the kettle when the reaction mixture had been heated to T°C. Then sodium carbonate was used to adjust the pH of reaction mixture to pH_1. Thereafter, the methylation reaction was continued for t_1 hours under constant temperature and stirring conditions. Subsequently, formic acid was used to reduce the pH of mixture to pH_2, then the polycondensation reaction took place and lasted for t_2 hours. The effects of pH, reaction time, molar ratio of formaldehyde to melamine and reaction temperature on MF's PS were investigated and the reaction conditions were shown in Table I.

Table I
Reaction conditions at the single-factor variable discussion.

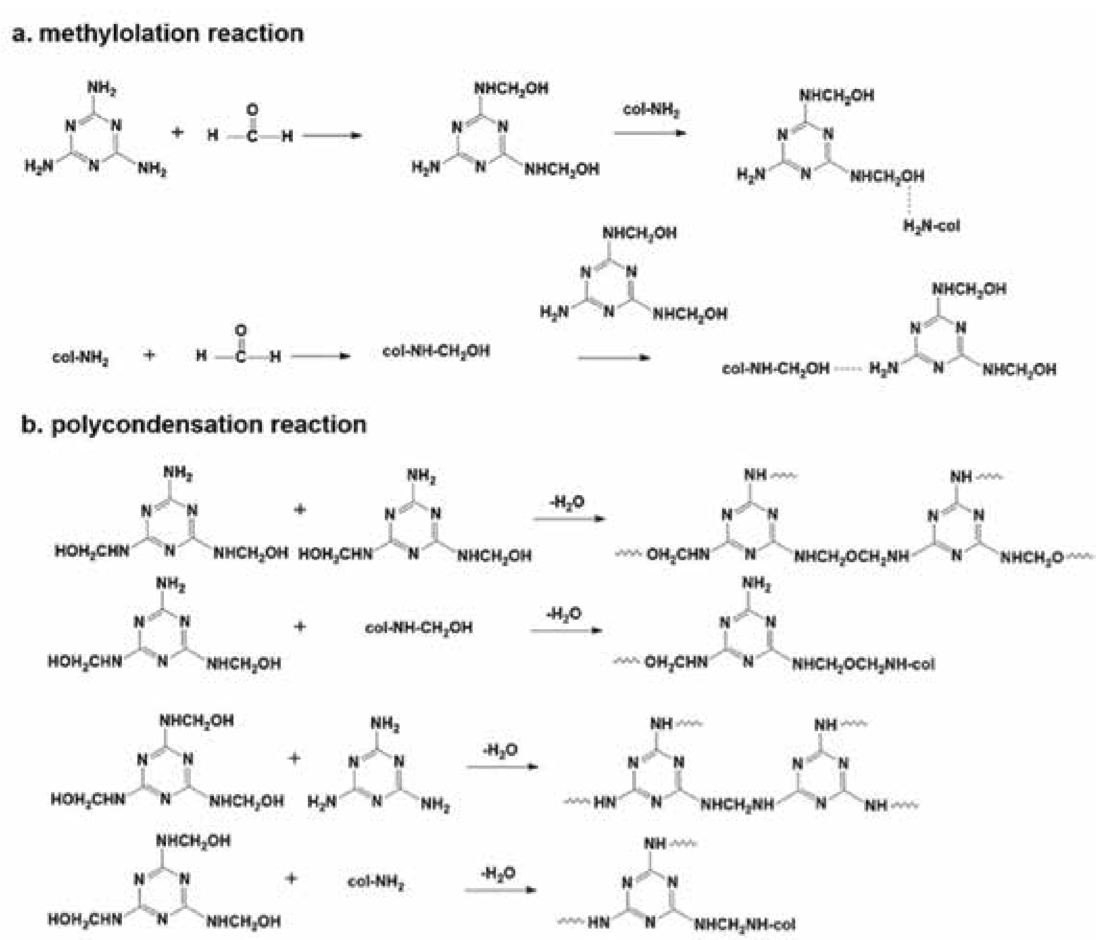
number	pH_1	t_1	pH_2	t_2	n(F/M) (mole ratio)	T
1	**X**[a]	3 h	none	none	3	45 °C
2	8.5	**X**[a]	none	none	3	45 °C
3	8.5	3 h	**X**[a]	2 h	3	45 °C
4	8.5	3 h	4.5	**X**[a]	3	45 °C
5	8.5	3 h	4.5	2 h	**X**[a]	45 °C
6	8.5	3 h	4.5	2 h	3	**X**[a]

X[a]: the parameter to be discussed.

pH_1: methylolation reaction pH; pH_2: polycondensation reaction pH; t_1: methylolation reaction time; t_2: polycondensation reaction time; n(F/M): the molar ratio of formaldehyde to melamine; T: reaction temperature.



Scheme 1. Possible reaction mechanism between melamine and formaldehyde.



Scheme 2. Possible reaction mechanism between collagen fiber and in-situ produced MF resin. (col means collagen)

Particle Size Measurement

The PS of the melamine-formaldehyde resin sample was determined using the Zetasizer Nano ZS90 equipment (Malvern Instruments Ltd., Malvern, UK). All the measurements were performed at 25°C with three times.

Tanning Trial

As given in Table II, *in-situ* tanning trials were carried out on bated goat skin with melamine and formaldehyde. The amounts of materials used in tanning process were based on 130% of the bated skin weight. Reaction conditions at the single-factor variable discussion were displayed in Table I. Moreover, Scheme 2 showed the possible reaction mechanism between the collagen and MF resin.

Assessment of Properties of Tanned Leathers

Thermal Stability Measurement of Leathers

The wet shrinkage temperature (T_s) of leather samples were measured by a MSW-YD4 shrinkage meter from Yangguang Research Institute of Shanxi University of Science and Technology according to Chinese Industrial Standard (QB/T 2713-2005).

Differential scanning calorimetric analysis was performed using a DSC calorimeter apparatus (Netzsch DSC 200 PC, German). The leather sample lyophilized (*ca.* 4 mg) was sealed in an aluminum pan with an empty aluminum pan as the reference and heated from 30 to 180°C with a constant heating rate of 10°C /min under a nitrogen flow.

Morphology Observation of Leathers

The cross-section morphologies of leather samples were observed using a field-emission scanning electron microscopy (FE-SEM, JSM-7500F, JEOL, Japan). The samples were made electrically conductive by gold-sputtered treatment and the images were observed in high vacuum mode.

Thickness Measurement of Leathers

The thickness of leather samples were measured by a desktop thickness gauge (ZY-9002-A), supplied by Zhuoyue Equipment Co., Ltd (Dongguan, China) and the thickening rate of the tanned leather compared with the bated skin was calculated according to the following formula.

$$\text{Thickening rate}(\%) = \frac{d_1 - d_0}{d_0} \times 100\%$$

d_0 represents the average thickness of the bated skin, d_1 represents the average thickness of the tanned leather.

Table II

***In-situ* tanning process with melamine and formaldehyde**

Process	Chemical	Offer/%	Temp./ °C	pH	Time/min	Remark
Tanning	Water	100	T			
	Melamine	3×3			30×3+90	
	Formaldehyde	5.792×n(F/M)*				
	$NaHCO_3$/ Na_2CO_3			pH_1	t_1	
	HCOOH			pH_2	t_2	Drain
Washing	Water	200	25		10	
Fatliquoring[a]	Water	100	50		10	
	GLH	3×2			15+45	Drain
Washing[a]	Water	200	25		10	

[a] Fatliquoring and [a] washing process were carried out for comparing the difference in mechanical properties.

$$* \quad \frac{m(\text{formaldehyde})}{m(\text{benchmark})} = \frac{n(\text{F/M}) \times \dfrac{m(\text{mela min e})}{M(\text{mela min e})} \times M(\text{formaldehyde})}{m(\text{benchmark}) \times 0.37} = [5.792 \times n(\text{F/M})]\%$$

Whiteness Measurement of Leathers

The whiteness measurements of the leather samples were performed by the chromatic aberration meter (X-RITE 8200) with illuminant D_{65} and 10° view angle supplied by Tong xing jia Electronic Co., Ltd (Shenzhen, China). The whiteness of samples and their color differences (ΔE) with the white standard were evaluated according to the CIE Lab measuring system.[20]

Mechanical Performance Measurement of Leathers

Tensile strength, tear strength and elongation at break were carried out for the fatliquored leather samples both along and across the backbone line. The leather samples were placed for 24h under 20±2°C and relative humidity of 65±5% before measurement, then their mechanical properties were measured on GT-AI-7000S tension machine (Gaotie Detection equipment co., Ltd., China) according to Chinese Industrial Standard (QB/T 1873-2004).[21]

Results and Discussion

Parameters Affecting the Particle Size of MF Resin Tanning Agent

Effect of pH on the MF Tanning Agent's PS

The formation of MF Resin can be divided into two stages, methylolation and polycondensation reaction. The effect of methylolation pH (pH_1) and polycondensation pH (pH2) variation on the PS of MF resin tanning agent were presented in Figure 1.

It can be seen from Figure 1(a) that the peak of the maximum proportion of the tanning agent's PS was approximately 250 nm. The PS was small because the melamine was more likely to react with formaldehyde to form small hydroxymethyl melamine under alkaline conditions.[22] Figure 1 (b) revealed that the tanning agent's PS changed from 250 nm or so for pH 8.5 to above 3000 nm for pH 4.5, showing a rapidly increase with the decrease of pH value. This phenomenon was ascribed to the occurrence of macromolecules with methylene bonds and methylene ether bonds produced by polycondensation reaction under acidic conditions (Sheme1).[23] In the first stage, formic acid is easily produced by the Cannizzaro reaction with the pH higher than 8.5, affecting the degree of methylolation reaction.[24] So the appropriate pH value of methylolation reaction was about 8.5, in which case the particle was small and stable. In addition, the idea pH in polycondensation stage was 4.5 for the formation of large tanning agent particles in this case. In practical tannage, the small particles produced by methylolation reaction will become larger via polycondensation triggered by decreasing the pH value slowly.

Effect of Reaction Time on the MF Tanning Agent's PS

During methylolation reaction, once the suspended melamine was fully dissolved, indicating that the methylolation reaction had been basically completed. And the PS of tanning agent changed with the prolongation of reaction time. Figure 2 displayed the effect of reaction time on the PS of MF tanning agent.

As presented in Figure 2(a), the PS of the product was more than 300 nm in the initial stage of methylolation reaction (1h), which was possibly due to the fact that a small amount of melamine was not dissolved and suspended in the system. After 3 hours of reaction, the PS of the melamine derivative did not change significantly. This was because the hydroxymethyl melamine

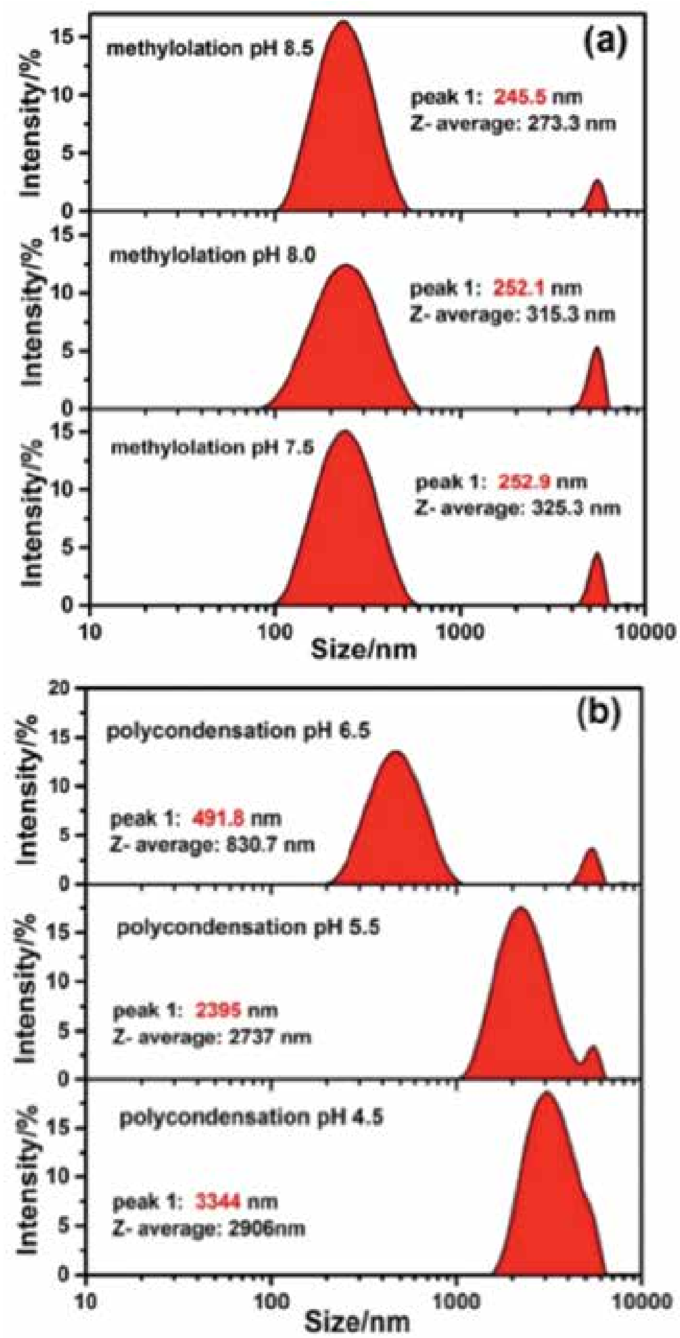


Figure 1. Effect of pH on the MF Tanning Agent's PS. (a) methylolation reaction (n(F/M)= 3.0, T=45°C, t_1= 3 h); (b) polycondensation reaction (T=45°C, t_2= 2 h).

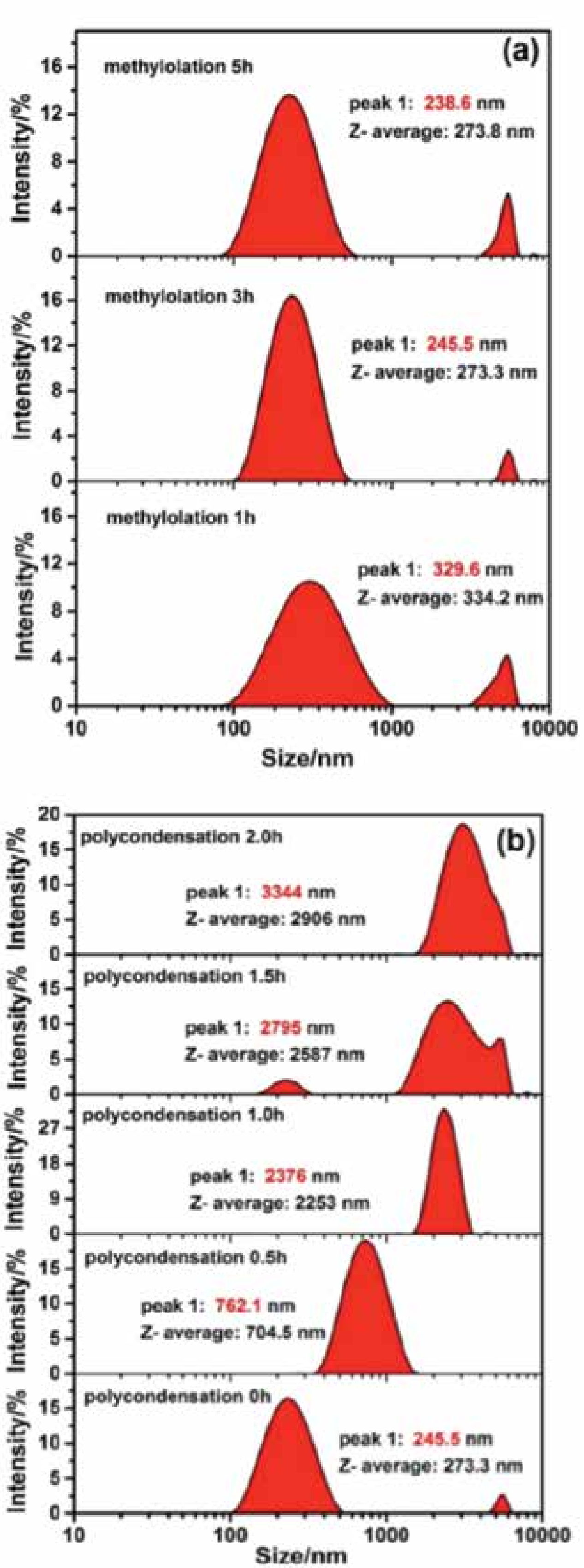


Figure 2. Effect of Reaction Time on the MF Tanning Agent's PS. (a) methylolation reaction–(n(F/M)= 3.0, T=45°C, pH_1 =8.5); (b) polycondensation reaction (T=45°C, pH_2=4.5).

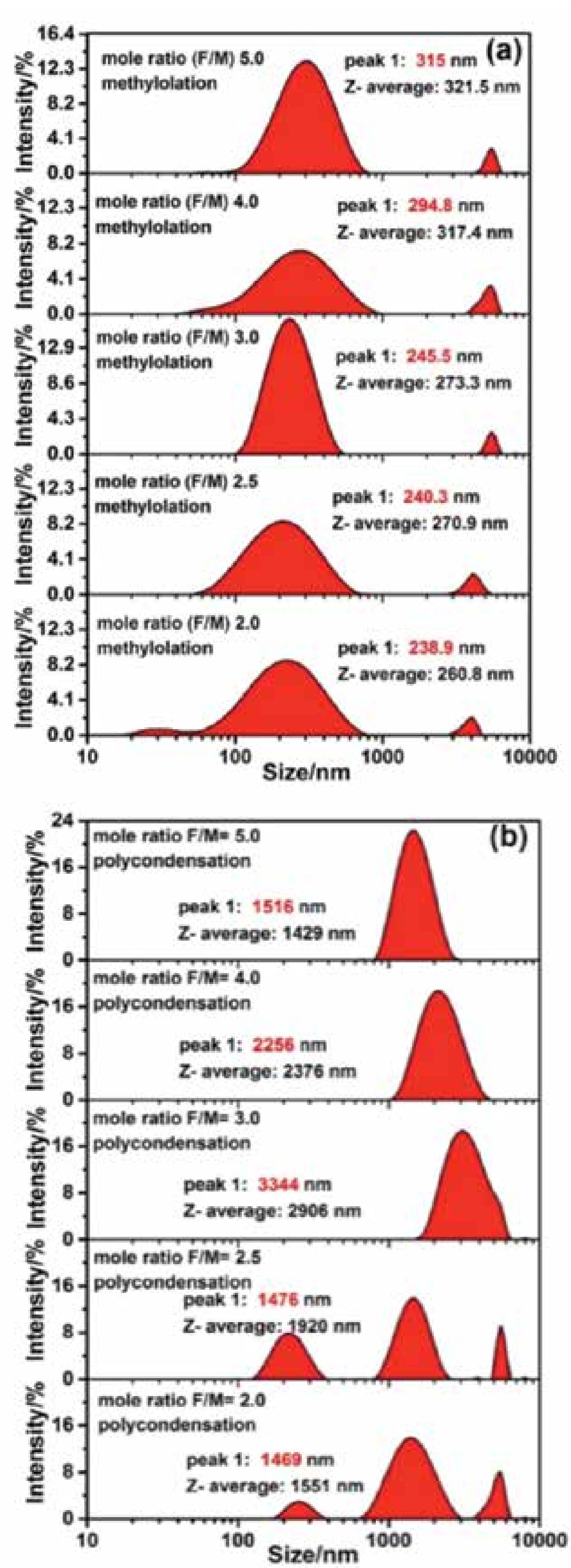


Figure 3. Effect of Molar Ratio of Formaldehyde to Melamine on the MF Tanning Agent's PS. (a) the particle size of tanning agent at end of mehylolation reaction. (T=45°C, pH_1 =8.5, t_1= 3 h); (b) the particle size of tanning agent at end of polycondensation reaction. (T=45°C, pH_2=4.5, t_2=2 h).

was relatively stable and not prone to undergo polycondensation reaction to form macromolecules under alkaline conditions. According to Figure 2 (b), the PS of MF tanning agent increased rapidly with the extension of polycondensation time. This mainly because the polycondensation degree of hydroxymethyl melamine increased with prolonging reaction time.[25,26] From the above analysis we found that tanning agent's PS was smaller in the methylation reaction stage and increased rapidly when the polycondensation reaction lasted for 1h ~ 2h.

Effect of Molar Ratio of Formaldehyde to Melamine on the MF Tanning Agent's PS

In theory, the six active hydrogen atoms of melamine molecules can all react with formaldehyde to form hydroxymethyl groups. With different molar ratio of formaldehyde to melamine, the product contains different numbers of hydroxymethyl groups. Therefore, the mole ratio can influence the structure of MF resin tanning agent that in turn affect its PS. Figure 3 presented the effect of molar ratio of formaldehyde to melamine on MF resin tanning agent's PS.

As depicted in Figure 3, the PS of the tanning agent was small and showed little changes with the increase of molar ratio of formaldehyde to melamine in the methylolation stage. Nevertheless, in the polycondensation stage, the PS showed an increasing tendency with increasing the mole ratio of formaldehyde to melamine when the molar ratio was less 3. This phenomenon might be owing to the increased active hydroxymethyl groups on the hydroxymethyl melamine resulting from higher mole ratio of formaldehyde to melamine, which was beneficial for polycondensation of hydroxymethyl melamine. When the mole ratio of formaldehyde to melamine was greater than 3, a slight decrease in PS can be observed, this might be because the steric hindrance of multi-hydroxymethyl groups hindered polycondensation reaction. In accordance with previous work, the optimum mole ratio used in the synthesis of MF resin tanning agent was 3.[27]

Effect of Reaction Temperature on the MF Resin Tanning Agent's PS

In general, the shrinkage temperature of the bated skin is about 50°C. In order to avoid the shrinkage of the raw skin in early tanning process, the reaction temperature was controlled to low 45°C. The effect of reaction temperature on MF resin tanning agent's PS was shown in Figure 4.

The study of reaction kinetics indicated that the reaction rate constant of melamine and formaldehyde was a function of temperature,[28] so higher temperature can accelerate the reaction rate, furthermore, influence the PS evolution. It can be seen from Figure 4 that the MF resin's PS in the methylolation stage showed little changes with the increase of temperature, but showed large increase in polycondensation stage, which indicated that higher temperature promoted the reaction rate and the increase of PS mainly relied on the polycondensation reaction. Thus, the reaction temperature of 45°C is a suitable temperature to enhance the tanning agent's PS.

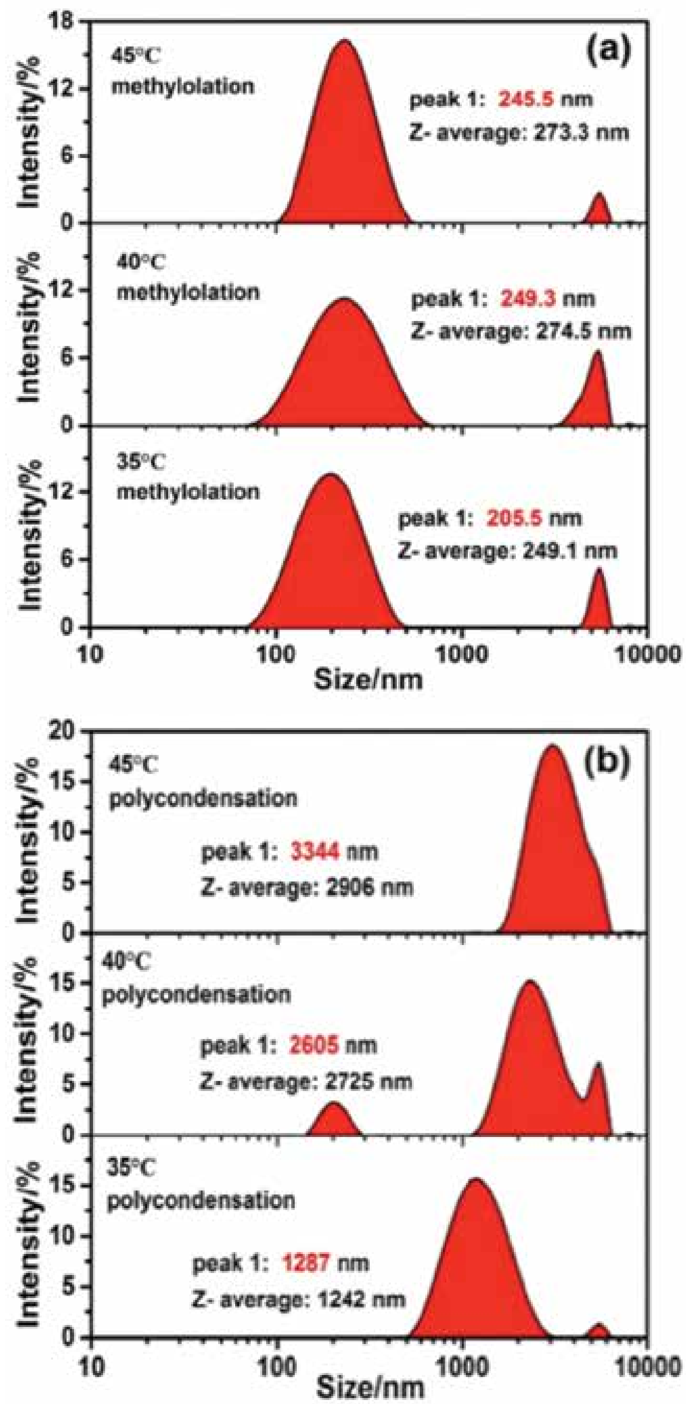


Figure 4. Effect of Reaction Temperature on the MF Tanning Agent's PS. (a) the tanning agent's PS at end of mehylolation reaction. (n(F/M)= 3.0, pH_1 =8.5, t_1= 3 h); (b) the tanning agent's PS at end of polycondensation reaction. (pH_2=4.5, t_2=2 h).

The Effect of Tanning Agent's PS on Properties of Tanned Leather

Thermal Stability of Tanned Leather

In an attempt to identify the effect of MF's PS on the thermal stability of tanned leather, the wet shrinkage temperatures (T_s) variations and DSC curves of leather tanned by MF resin with different PS were compared and presented in Figure 5 and Figure 6, respectively. The experimental conditions were listed in Table I.

In addition to the wet shrinkage temperature (T_s), the denaturation temperature (T_d) in the DSC curve of leather sample was also employed as an indicator of the thermal stability of the leather.[29-31] It was found from Figure 5 that the leather samples exhibited low shrinkage temperature after being tanned with small tanning agent particles (about 250 nm) in the methylolation stage. But in the polycondensation reaction stage, with the decrease of polycondensation reaction pH, the increase of temperature, time and molar ratio of formaldehyde to melamine, the wet shrinkage temperature of the sample increased continuously (T_s increased from 91°C to 99°C), which was roughly consistent with the increasing trend of tanning agent's PS. Meanwhile, the changing trend of denaturation temperature (T_d) is as the same as wet shrinkage temperature. We can attribute the above phenomena to the following reasons: In the early stages of tanning, the hydroxymethyl melamine with small size were *in-situ* produced and evenly distributed in the interstices of collagen fibers; and in the latter stage of tanning, the polycondensation reaction was initiated to generate large tanning agent particles by reducing the reaction pH. These large size MF particles can react with amino, hydroxyl or methylol groups (produced by reaction between formaldehyde and collagen amino) of collagen fibers easily via covalent bonds and hydrogen bonds, thus increasing the thermal stability of tanned leather.[19]

From the above analysis we can obtain the optimum conditions for *in-situ* tanning with MF resin as follows: In methylolation reaction stage, the temperature was 45°C, the molar ratio of formaldehyde to melamine was 3, the pH was 8.5 and the reaction time was 3 h; In the polycondensation stage, the pH was 4.5 and the reaction time was 2 h.

In order to specifically elucidate the effect of tanning agent's PS evolution on other tanning properties, we further explored the change of tanning properties before and after polycondensation reaction, while other conditions were copied from the optimality mentioned above.

Cross-Section Morphologies of Tanned Leathers

The cross-section morphology difference between the leather samples can be distinguished by scanning electron micrography

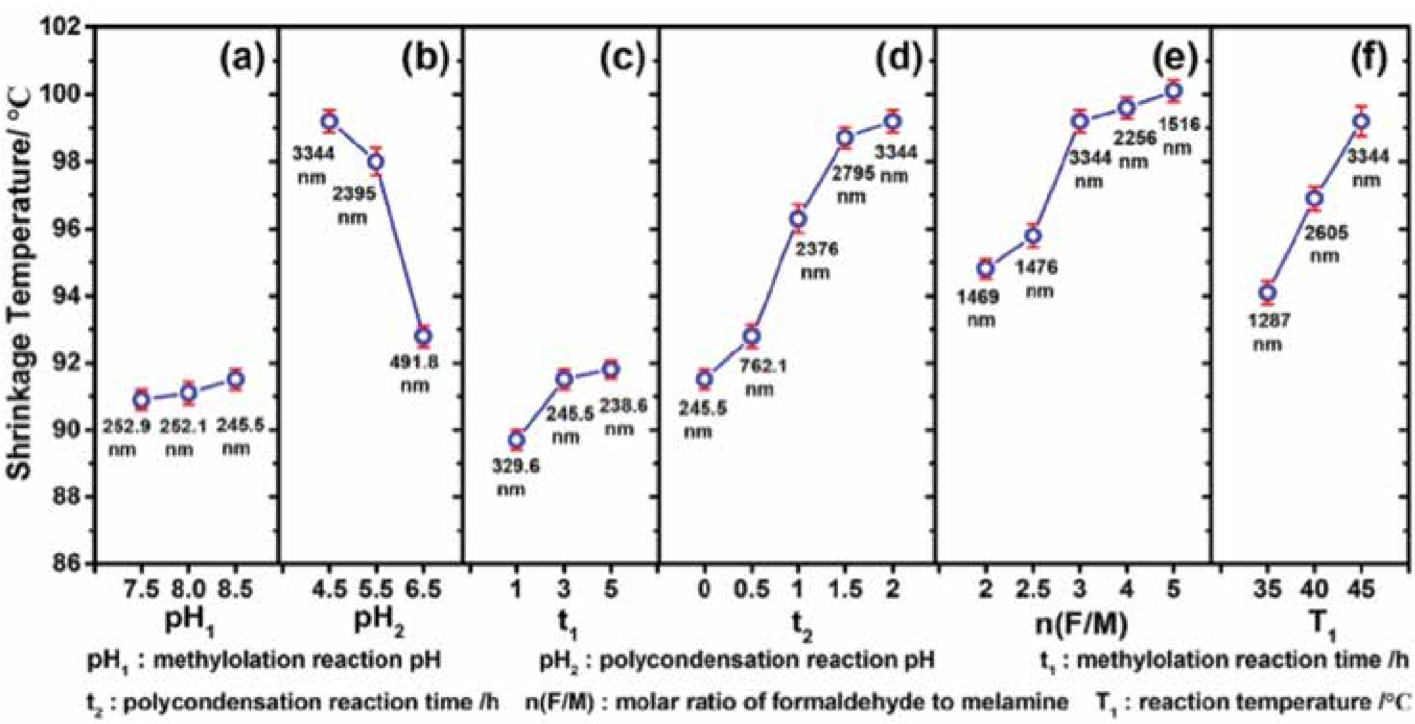


Figure 5. Wet shrinkage temperature of tanned leather. (a) different methylolation pH (pH_1), n(F/M)= 3.0, T=45°C, t_1= 3 h; (b) different polycondensation pH (pH_2), n(F/M)= 3.0, T=45°C, pH_1 =8.5, t_1= 3 h, t_2= 2 h; (c) different methylolation time (t_1), n(F/M)= 3.0, T=45°C, pH_1 =8.5; (d) different polycondensation time (t_2), n(F/M)= 3.0, T=45°C, pH_1 =8.5, t_1= 3 h, pH_2=4.5; (e) different molar ratio of formaldehyde to melamine (n(F/M)), T=45°C, pH_1 =8.5, t_1= 3 h, pH_2=4.5, t_2=2 h; (f) different reaction temperature (T), n(F/M)= 3.0, pH_1 =8.5, t_1= 3 h, pH_2=4.5, t_2=2 h.

observation (Figure 7). In sample 1(figure 7(a)), the fiber bundles were bound together, whilst the fiber bundles of sample 2 were more dispersed (figure 7(b)). This suggested that the multi-point crosslinking between large tanning agent particles and collagen fiber bundles was established. As a result, the space between collagen fibers was opened and the final leather exhibited more even open-up fiber structure.

Thickening Rate of Tanned Leathers

The PS of tanning agent also influenced the fullness of leather evaluated by its thickening rate. From Figure 8, it was found that the thickening rate of the part near to the abdomen was higher than that of the part near to the back line, showing selective filling effect of MF tanning agent. As we all know, the collagen fibers in the abdomen portion are more loosely woven than that of the back position, so it is easier for tanning agent to fill the space between fibers in the abdomen portion, resulting in better filling effect. No matter in any position, the thickening rate and fullness of leather sample 2 was greater than that of leather sample 1 for the better filling property of large tanning agent particles.

Whiteness of Tanned Leathers

The leather tanned with melamine-formaldehyde resin possess high whiteness and excellent light fastness, which can be used to prepare light colored leather.[32] In the CIE Lab method, the L coordinates is related to lightness.[33] Figure 9 presented the reflectance curves and color differences of the leather samples. It can be seen that the reflectance curve of leather sample 2 tanned with large particles was higher and flatter compared with that of

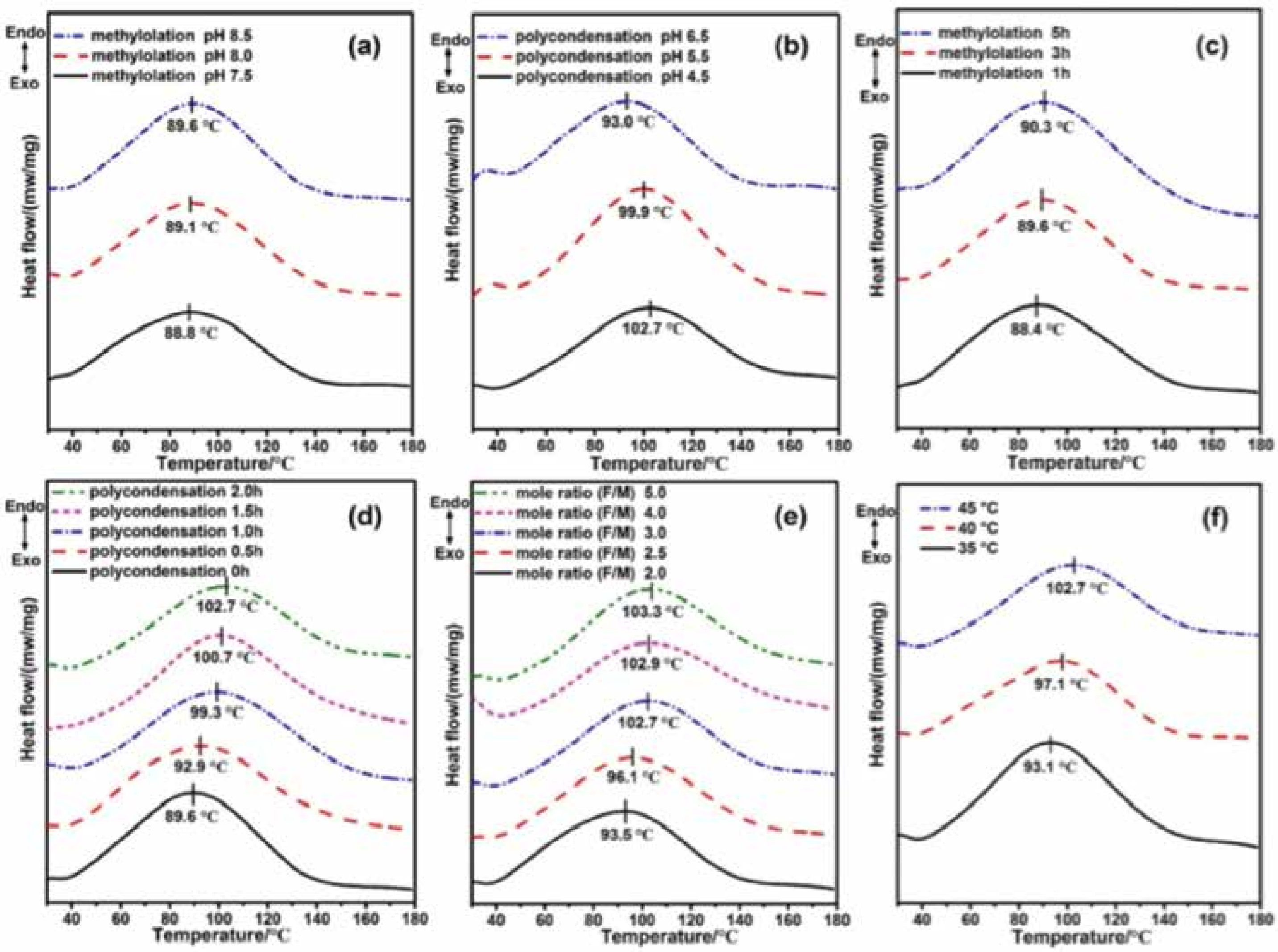


Figure 6. DSC curves of tanned leather. (a) different methylolation pH (pH_1), n(F/M)= 3.0, T=45°C, t_1= 3 h; (b) different polycondensation pH (pH_2), n(F/M)= 3.0, T=45°C, pH_1 =8.5, t_1= 3 h, t_2= 2 h; (c) different methylolation time (t_1), n(F/M)= 3.0, T=45°C, pH_1 =8.5; (d) different polycondensation time (t_2), n(F/M)= 3.0, T=45°C, pH_1 =8.5, t_1= 3 h, pH_2=4.5; (e) different molar ratio of formaldehyde to melamine (n(F/M)), T=45°C, pH_1 =8.5, t_1= 3 h, pH_2=4.5, t_2=2 h; (f) different reaction temperature (T), n(F/M)= 3.0, pH_1 =8.5, t_1= 3 h, pH_2=4.5, t_2=2 h.

sample 1 tanned with small particles. This indicated that the shade of leather sample 2 was lighter than sample 1,[34] which can also be confirmed by larger L value of sample 2 (93.55) in comparison with that of sample 1 (85.23). The color difference value (**Δ**E) of sample 2(3.6) was smaller than that of sample 1(12.26), indicating that color of sample 2 was closer to that of the reference whiteboard, that is, sample 2 was whiter than sample 1. This might be attributed to the better uptake of tanning agent by the sample 2.

Mechanical Performance of Tanned Leathers

The elongation at break, tensile strength and tear strength of leather samples were measured and shown in Figure 10. It was noticed that the leather sample 2 tanned with large tanning particles showed a slight reduction in tensile strength and teas strength compared with sample 1 which was tanned with small tanning particles. This was because large particle tanning agent with strong filling property enlarged the weave angle of fibers and reduced the tightness of fiber bundles, leading to tear strength decrease of sample 2. Besides, the fibers orientation of sample 2 was poor compared with that of sample 1, that meant the fibers of sample 2 were not capable of transferring the stress uniformly when the stress got accumulated, which resulted in low tensile strength.[34] However, the elongation at break of sample 1 was lower than that of sample 2, this may be because cohesive and stiff fiber bundles of sample 1 (as shown in Fig. 7) reduced its resilience and toughness.[35]

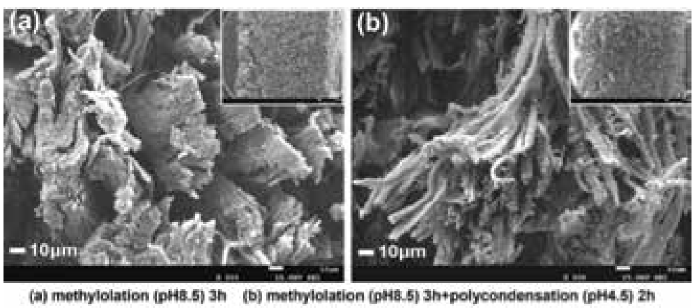


Figure 7. SEM micrographs of cross section (50× and 500×) of two tanned leathers. (a) sample 1, tanned with small PS tanning agent; (b) sample 2, tanned with small PS tanning agent followed by large PS tanning agent.

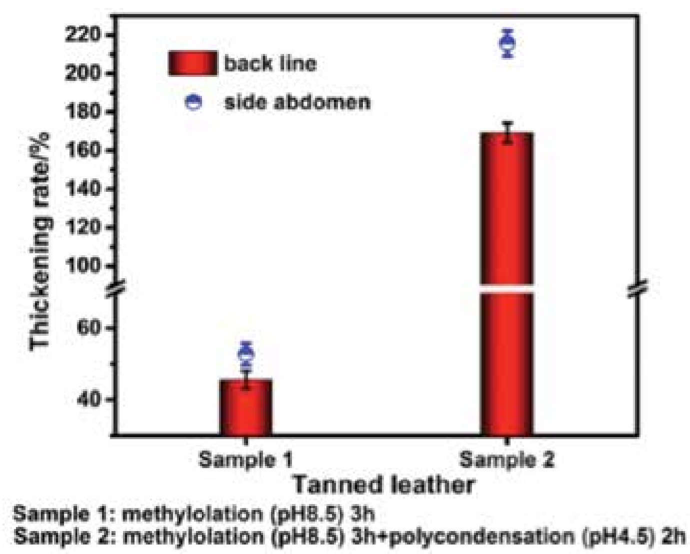


Figure 8. Thickening rate of the two leather samples. (Sample 1: tanned with small PS tanning agent; Sample 2: tanned with small PS tanning agent followed by large PS tanning agent.)

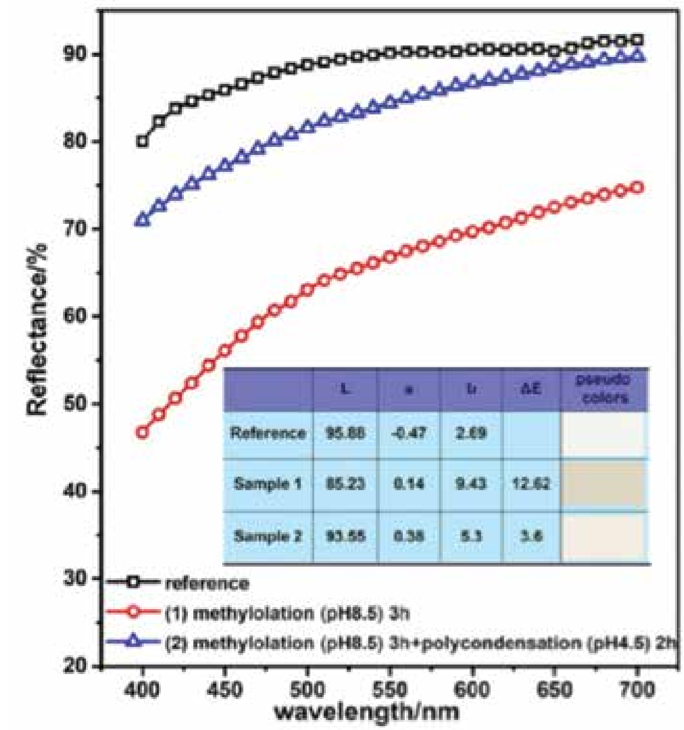


Figure 9. The reflectance curves and color differences of the two leather samples. (Sample 1: tanned with small PS tanning agent; Sample 2: tanned with small PS tanning agent followed by large PS tanning agent.)

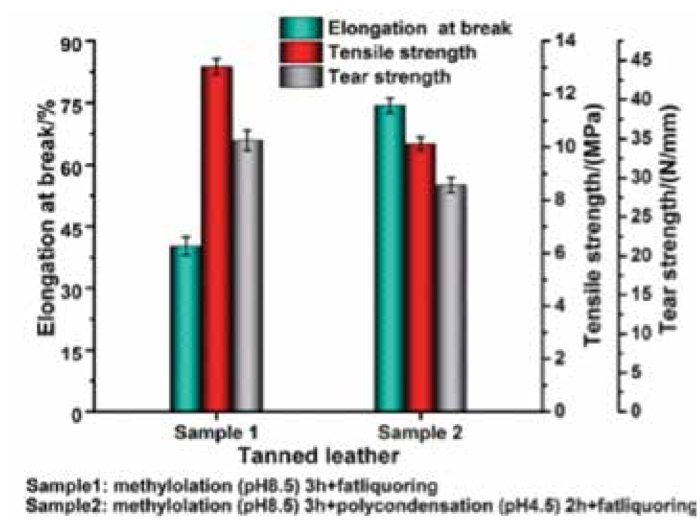


Figure 10. Mechanical performance of two leather samples. (Sample 1: tanned with small PS tanning agent; Sample 2: tanned with small PS tanning agent followed by large PS tanning agent.)

Conclusions

Tanning with MF resin was divided into its methylation and polycondensation reactions inside the skin. The optimum reaction parameters for the methylation stage were at a pH of 8.5, a molar ratio of formaldehyde to melamine 3: 1, a temperature of 45°C and a reaction time of 3 hours. The resultant average value of PS for this MF resin at the methylation stage was less than 300 nm. This low range of PS values produced inside the skin had a minimal tanning effect. The PS of MF resin increased rapidly during the polycondensation stage by lowering reaction pH and increasing the molar ratio of formaldehyde to melamine. The preferred extent of polycondensation of MF resin among the collagen fibers was done at a pH of 4.5, a reaction temperature of 45°C for a total of two hours. The performance of leather made from only the methylation reaction of MF resin was poor. It was flat or empty, and showed a low shrinkage temperature which meant a minimal tanning effect. Its mechanical strength was not acceptable as evidenced by a low-valued elongation at break. By contrast, leather which was prepared by methylation and quickly followed by adequate polycondensation reactions was fully acceptable. It was white, full and mechanically strong due to a high value elongation at break. It also had a high shrinkage temperature which signified adequate tanning effect. Thus, the large particles of MF resin are believed to be more inclined to establish multi-reaction points with collagen fiber bundles, and consequently gave this enhanced performance of leather. Our *in-situ* approach to tanning overcame the established difficulty of traditional MF resin tanning agents penetrating the skin. Moreover, the synthesis conditions can be readily tweaked so as control and adjust PS of MF resin and thus maximize the efficiency of its tanning. Our research will continue to reveal the scope of the tanning mechanism of this *in-situ* MF resin and thus provide a reference for putting forward a simpler and more efficient tanning methods in the future.

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