

# A NOVEL CHROMIUM-FREE TANNING PROCESS BASED ON *IN-SITU* MELAMINE-FORMALDEHYDE OLIGOMER CONDENSATE

by

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## ABSTRACT

To manage the environmental impacts of chrome tanning, a burgeoning option lies in seeking alternatives that reproduce the high hydrothermal stability and retain the versatility of chromium salts. In this study, a novel chromium-free tanning process based on *in-situ* condensate melamine-formaldehyde oligomer was reported. Instead of using prepared melamine-formaldehyde syntan, which inevitably contained post-condensates with compromised penetration capability and reactivity, melamine and formaldehyde monomers were first allowed to penetrate evenly into bated hides and then condensation was triggered *in-situ*. Total organic carbon (TOC), total nitrogen (TN), Fourier transform infrared (FTIR), and isoelectric point (IP) analysis demonstrated these *in-situ* condensate oligomers covalently reacted with amino or hydroxyl residues, introducing rigid and stable chemical crosslink between collagen chains. Consequently, the hydrothermal stability of the tanned leather was significantly enhanced, evidenced by thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC) and a shrinking temperature ( $T_s$ ) approaching 93°C. In addition, scanning electron microscope (SEM) observation indicated that the *in-situ* tanned leather exhibited smoother grain, more even and much looser fiber structure compared with control, which was tanned by traditional melamine-formaldehyde syntan. According to these results, the *in-situ* condensation strategy developed in this study could be employed as an efficient chromium-free tanning, which eliminated the adverse effects of post-condensates in traditional melamine-formaldehyde syntan while exhibiting improved tanning efficiency.

## INTRODUCTION

Tanning involves a process that introduces crosslink between collagen chains to permanently alter their structure so that they can be preserved and irreversibly converted into useful leather. Up until now, there have been many different methods for tanning hides, such as chrome tanning, vegetable tanning, aldehyde tanning, oil tanning, synthetic organic tanning, etc.<sup>1</sup> Among these techniques, chromium salt tanning system rapidly took its place in the commercial world shortly after its discovery in 1858, and remains the predominating tanning method in global leather industry. However, despite many technical advantages associated with this tanning method, traditional chrome tanning is under continuous pressure currently from environmental perspectives, including a global shortage of chrome source, potential carcinogenicity of hexavalent chrome and a low combination ratio of chrome in the tanned leather.<sup>2</sup> In addition, the presence of chromium in leather wastes also represents a potential hazard due to the possibility of Cr (III) being converted to its toxic state, Cr (VI), making re-utilization of chrome-tanned leather wastes difficult.<sup>3</sup> Over the past decades therefore, there has been a huge surge of interests in seeking alternatives that are environmentally sound while retaining the versatility of chrome tanning.<sup>4-10</sup>

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Synthetic tanning agent is a type of polymer with reactive groups to crosslink collagen chains, which confers all the properties currently provided by chromium salts and offers the potential for continuing improvements in processing and leather performances. Especially, melamine-formaldehyde resin is a heterocyclic, weak alkaline syntan frequently used for leather re-tanning. As is well established, such organic syntan is normally synthesized in a conventional manner, by a two-step alkaline condensation of melamine with formaldehyde. In the first step, the amino groups in melamine react with formaldehyde under alkaline condition, producing an intermediate called methylol-melamine. Subsequently, condensation reaction occurs between several methylol-melamines to form ether-bridged oligomer. In this case, self-condensation is so strong that the resultant melamine-formaldehyde resin is unstable in water phase, so a spray-drying process is necessary to stop further self-condensation. In the powdery melamine-formaldehyde resin, residual methylol terminals have a potential to react with amino or hydroxyl residues located in collagen, introducing crosslinks between collagen chains to confer hydrothermal stability. In addition to tanning effect, it is equally important that the melamine-formaldehyde syntan can also serve as filling agents to endow the tanned leather with plumpness, as well as compactness, especially for belly and shank regions. In comparison with chrome-tanned leather, another advantage associated with melamine-formaldehyde resin tannage lies in the white color of the resultant leather as well as its excellent light fastness.<sup>11</sup> However, according to previous reports, the shrinkage temperature of commercial melamine-formaldehyde resin tanned leather was only approximately 70°C, considerably lower than that of chrome-tanned leather which usually exceeds 120°C. This is mainly because the self-condensation consumes most hydroxymethyls during polymerization and storage, on one hand, increasing molecular size and destabilizing the syntan; on the other hand, making the syntan difficult to penetrate evenly into the hides, compromising its tanning efficiency and resulting in hardness/cracked grain.

In view of those disadvantages associated with traditional melamine-formaldehyde syntan, a novel chromium-free tannage based on *in-situ* condensate melamine-formaldehyde oligomer was developed in the present study. Instead of tanning the hides using prepared melamine-formaldehyde syntan, we explored the feasibility of triggering *in-situ* condensation reaction between melamine and formaldehyde monomers directly within the collagen fibers, in an attempt to retain high tanning efficiency of the oligomer when crosslinking the collagen. Such *in-situ* condensation strategy could also avoid the occurrence of self-condensation, and overcome the difficulty of uneven penetration associated with traditional melamine-formaldehyde syntan. In addition, pickling process was not necessary before this novel

chromium-free tannage, eliminating discharge of effluents containing a large number of environmentally hazardous salts and hydrochloric acids. The tanning mechanism of such *in situ* condensation strategy was investigated based on experimental results from total organic carbon (TOC), total nitrogen (TN), Fourier transform infrared (FTIR) spectroscopy, and isoelectric point (IP) measurements. In addition, the hydrothermal stability and fiber structure of the tanned leather were also evaluated, employing formaldehyde-tanned or traditional melamine-formaldehyde resin-tanned leather as control. The aim of this study is to provide an alternative strategy to utilize melamine-formaldehyde oligomer, which is eco-friendly as a novel chromium-free tannage and allows more targeted and higher efficient tanning than traditional product.

## EXPERIMENTAL PROCEDURES

### Materials

Gelatin was purchased from Tianjin Bodi Chemical Co., Ltd. Goat raw hides used in this study were made in our laboratory. Melamine and formaldehyde were obtained from Chengdu Changzheng Co., Ltd. Glacial acetic acid, sodium bicarbonate, anhydrous ethanol, hydrochloric acid and sodium hydroxide of analytical grade were purchased from Chengdu Kelong Chemical Co., Ltd. Melamine formaldehyde syntan was obtained from BASF Co.

### Preparation of Modified Gelatin

First, gelatin and a certain quantity of deionized water were mixed to soak overnight in a three-necked flask with a water bath heating to dissolve. Then measured melamine was added into the flask gradually, and the reaction was stirred for 3 hours at 40°C in a water bath after the melamine was dissolved completely. Sodium bicarbonate was used to adjust the pH value to 8, measured formaldehyde was added and reaction was stirred in 45°C water bath for 3 hours. The final pH value was adjusted to 4.5 and the reaction continued for 2 hours. After completion of the reaction, removed product was precipitated in anhydrous ethanol and then wash it for 2-3 times by anhydrous ethanol to remove the unreacted melamine, dried at room temperature and collected for the analysis.

### TOC and TN Measurements

An Anatel TOC-2000 Organics Analyzer (Elementar Analysensysteme GmbH, Germany) was used to measure the TOC and TN of pristine gelatin and the modified one. Prior to analysis, the sample was dissolved in deionized water and diluted to a concentration of approximately 0.1 g/L. Then, 1 mL sample solution was injected into the analyzer for measurement.

### FTIR Analysis

Fourier transform infrared spectra (FTIR) were collected at ambient temperature using a Nicolet iS10 FTIR spectrometer.

A pure KBr pellet was used as reference and its spectrum was subtracted from the sample spectra to suppress spectral artifacts caused by KBr impurities and water.

### IP Measurements

The IP of pristine gelatin and the modified one in aqueous solution was determined using the Zetasizer Nano ZS90 equipment (Malvern Instruments, Worcestershire, UK). The IP was determined as the pH value, at which the Zeta potential of the sample solution was zero under the applied electric field.

### TGA Analysis

Thermogravimetric analysis (TGA) was carried out in a NETZSCH TG 209 F1 analyzer equipped with a TASC 414/3 thermal analysis controller with a rate of 5°C/min under N<sub>2</sub> atmosphere.

### Tanning of Bated Goat Hides

Matched pieces of hide samples (30 × 30 cm) were taken from the flank areas of a bated goat hide. The thickness of the sample was about 3.0 mm. The chemicals used in the following procedure were based on the weight of the hide sample. The tanning experiment was carried out as follows:

**TABLE I**

#### *In-situ* tanning process for bated goat hide.

Process	%	Chemical	Temp. °C	Time. min	pH
tanning	100	water	40	10	
	3	melamine		30	
	3	melamine		30	
	3	melamine		120	
	18	40% formaldehyde			
		NaHCO <sub>3</sub>			8
			45	180	
		CH <sub>3</sub> COOH			4.5
			45	120	

Finally, the tanned leather was allowed to stand overnight and dried naturally. For comparison, hide samples cut from the same areas were also tanned using either formaldehyde or commercial melamine-formaldehyde sytan. They were used as control in hydrothermal stability/color measurements and scanning electron microscope (SEM) observation.

### The Hydrothermal Stability

The denaturation temperature ( $T_d$ ) of the *in-situ* tanned leather was determined by using a NETZSCH Differential Scanning Calorimeter (DSC) 200 PC analyzer (5°C/min). The shrinkage temperature ( $T_s$ ) of leather sample was determined according to ASTM method D 6076-97. The bath was heated at a rate such that the rise in temperature was maintained at 3°C/min, and the temperature at the first definite sign of shrinking was recorded as  $T_s$ .

### Scanning Electron Microscope (SEM) Observation

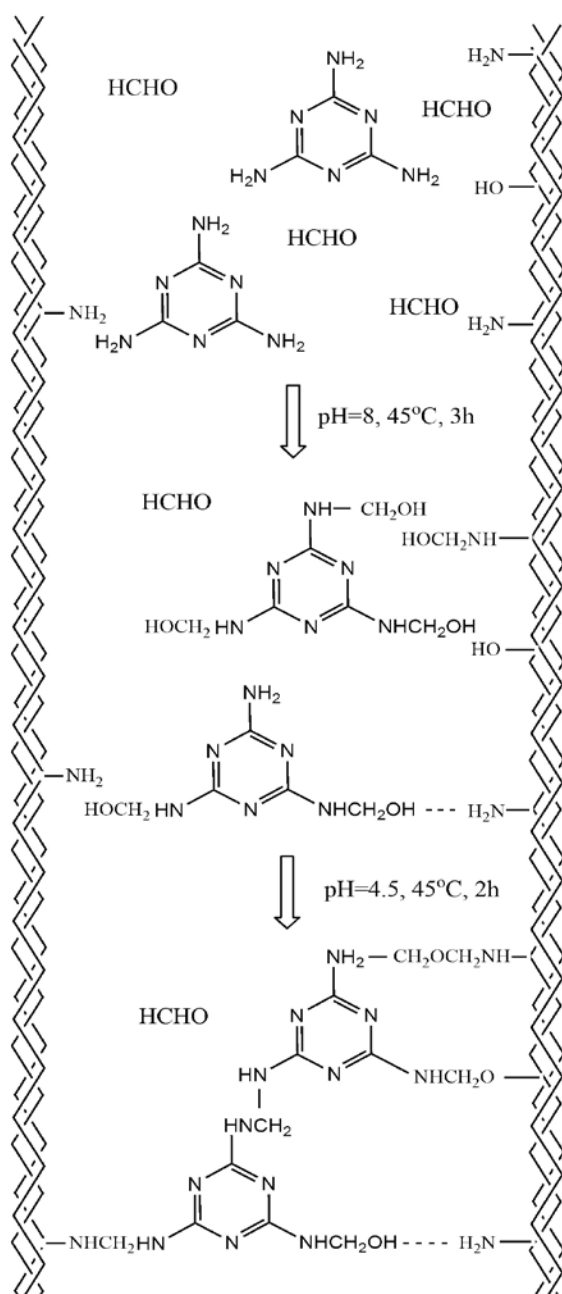
SEM (Hitachi Model S520, Japan) was employed to observe the surface and cross-section morphologies of the tanned leather. The cross sections were prepared by cryogenically fracturing the leather sample in liquid nitrogen.

## RESULTS AND DISCUSSION

### Tanning Mechanism

According to the *in-situ* condensation tannage developed in this study, which was schematically illustrated in Scheme 1, melamine and formaldehyde monomers were first allowed to penetrate evenly into the hides. With suitable pH value, the melamine would react with surrounding formaldehyde to produce highly reactive methylol-melamine. After that, condensation reaction between several methylol-melamine intermediates was triggered *in-situ* by adjusting the pH value of the float to 4.5, resulting in oligomers with reactive methylol terminals. Once these multiple methylol-containing oligomers were generated, they would react promptly with amino or hydroxyl groups in the hides, conferring high hydrothermal stability by forming rigid and stable crosslinking between collagen chains. On the other hand, residual methylol moieties could also form hydrogen bonds with amino groups in collagen, synergetically increasing the degree of crosslinking. In this *in-situ* condensation way, the tanning efficiency of melamine-formaldehyde resin was significantly enhanced, while excessive spatial extension of the oligomers generated was efficiently inhibited, thereby preventing the formation of post-condensates that could cause not only difficulty in penetration but also hardness/cracked grain. In addition, such *in-situ* condensation tanning process could be carried out directly on bated hides, which eliminated the pickling process for chrome tanning, thus decreasing the discharge of effluents containing a large number of environmentally-hazardous salts and hydrochloric acids.

Using gelatin as a model, the tanning mechanism proposed above could be efficiently evidenced by comparing the TOC, TN, FTIR spectrum and IP of gelatin before and after modification. First, the TOC and TN contents of the modified gelatin were measured to determine combination ability of the *in-situ* condensate melamine-formaldehyde oligomer<sup>[12]</sup>. As can be seen in Table II, the TOC and TN contents of pristine



Scheme 1. Possible tanning mechanism of *in-situ* condensate melamine-formaldehyde oligomer.

gelatin were only 61.1 mg/L and 32.2 mg/L, respectively. However, they increased to as high as 79.1 mg/L and 53.7 mg/L respectively after modification, exhibiting an increase by 29.5% and 65.7% respectively. This result indicated that abundant melamine-formaldehyde resin was present in the modified gelatin.

The covalent bonding between *in-situ* condensate melamine-formaldehyde oligomers and gelatin can be evidenced by FTIR and IP analysis. Figure 1 illustrated the FTIR spectra and the intensity changes in characteristic infrared absorption of pristine gelatin and the modified one. As for pristine gelatin, the absorption peaks at 1659  $\text{cm}^{-1}$ , 1454  $\text{cm}^{-1}$  and 1238  $\text{cm}^{-1}$

**TABLE II**  
The TOC, TN contents and IP value of gelatin after and before modification.

	Pristine Gelatin	Modified Gelatin
TOC (mg/L)	61.1	79.1
TN (mg/L)	32.2	53.7
IP	4.8	5.4

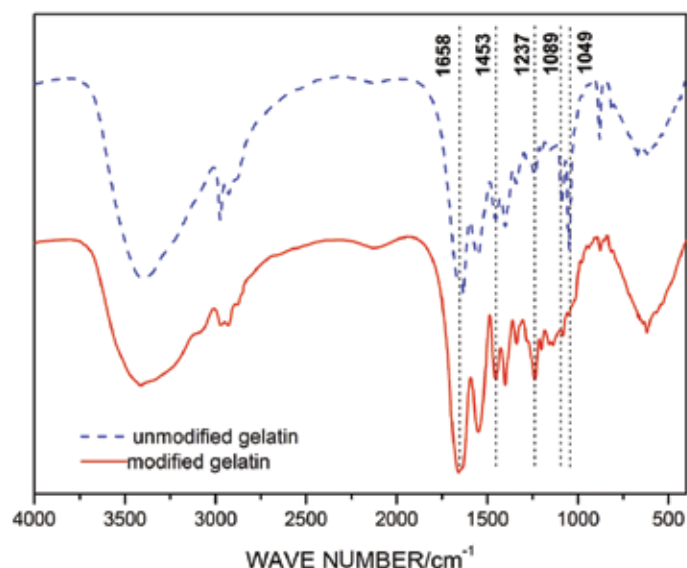


Figure 1. FTIR spectra of gelatin before and after modification.

were assigned to the stretch vibration of  $-\text{C}=\text{N}-$ ,  $-\text{CH}_2-$ , and  $-\text{C}-\text{O}-\text{C}-$  groups respectively. After modification with *in-situ* condensate melamine-formaldehyde oligomers, the intensities of these absorptions increased, while that corresponding to  $-\text{CH}_2\text{OH}$  decreased. This observation suggested that the methylol groups in melamine-formaldehyde oligomer reacted with the amino or hydroxyl groups in gelatin, resulting in formation of rigid and stable crosslinking between collagen chains. On the other hand, the change in IP value of gelatin after modification also provided valuable information regarding the chemical reaction between *in-situ* condensate melamine-formaldehyde and gelatin. In gelatin aqueous solution, the IP value was largely determined by the degree of dissociation of carboxyl and amino groups.<sup>13-14</sup> Therefore, the variations in carboxyl and amino contents could be efficiently revealed by measure the IP of the solution. The IP of pristine gelatin and the modified one were listed in Table II. It could be clearly seen that the IP value of the gelatin increased from 4.8 to 5.4 after modification. This result should be ascribed to the decrease of  $-\text{NH}_2$  content in gelatin, which had reacted with methylol groups generated in *in situ*-condensate melamine-formaldehyde oligomer.

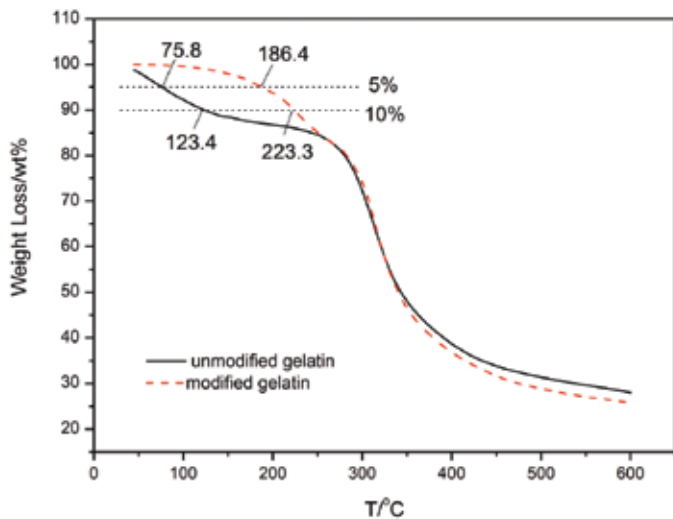


Figure 2. TGA thermograms of gelatin before and after modification.

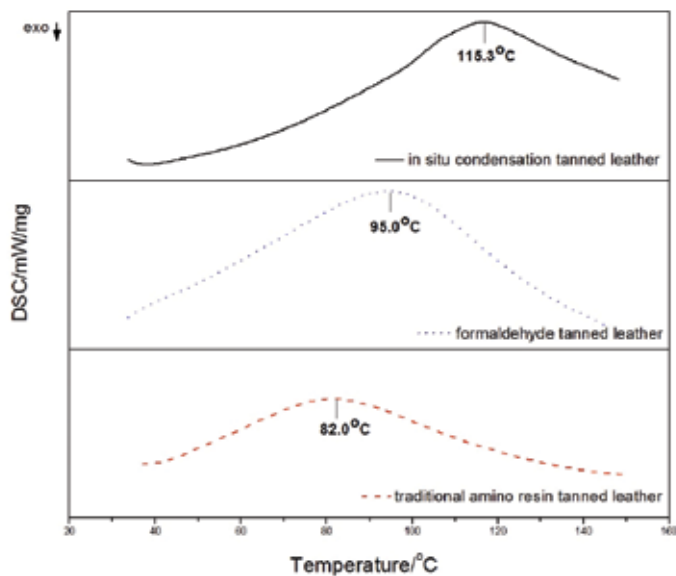


Figure 3. DSC thermograms of tanned leather.

### Hydrothermal Stability

The results discussed above confirmed multiple interactions between *in-situ* condensate melamine-formaldehyde oligomer and gelatin. As a consequence, the hydrothermal stability of the modified gelatin or leather could be efficiently enhanced. Figure 2 presents the TGA thermograms of pristine gelatin and one after modification. For pristine gelatin, the temperatures for 5 wt.% and 10 wt.% weight loss were approximately 75.8°C and 123.4°C, respectively. After modification with *in-situ* condensate melamine-formaldehyde oligomer, they increased significantly to 186.4°C and 223.3°C.

Figure 3 shows the DSC thermograms of tanned leather. In DSC analysis, the endothermic peak of a leather sample provided information about the denaturation of leather over a defined temperature range, and this parameter had been widely employed as an indicator of the hydrothermal stability of tanned leather subjected to different tanning agent treatments. As for formaldehyde and melamine-formaldehyde syntan tanned leather, the denature temperature ( $T_d$ ) were only 95°C and 82°C respectively. While the  $T_d$  of leather tanned by the *in-situ* condensate oligomer was found to be increased by almost 20°C and 33°C respectively, reaching 115.3°C. This significant increase indicated that the tanning efficiency of *in-situ* condensate melamine-formaldehyde oligomer was much stronger than formaldehyde alone. They had reacted covalently with functional groups in collagen chains, producing rigid and stable chemical crosslinking between collagen chains, thus conferring high hydrothermal stability to the resultant leather.

Similarly, the shrinking temperatures ( $T_s$ ) of formaldehyde and *in-situ* tanned leathers were also measured. The  $T_s$  of *in-situ* tanned leather reached  $93\pm 3^\circ\text{C}$ , shows stronger tanning efficiency compared with that of control, which was tanned with formaldehyde alone ( $80\pm 3^\circ\text{C}$ ) and traditional melamine-formaldehyde syntan ( $74\pm 3^\circ\text{C}$ ). Although the  $T_s$  of the *in-situ* tanned leather was still lower than that of traditional chrome-

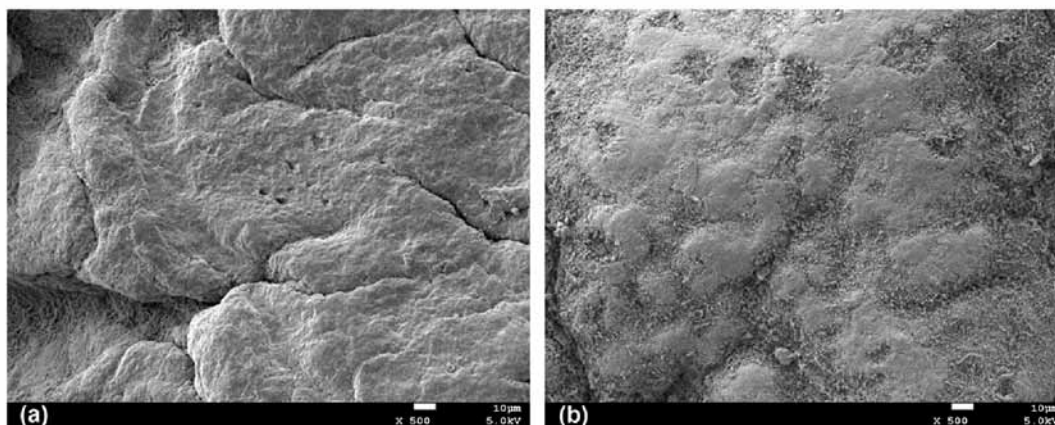


Figure 4. Scanning electron microscopic image of grain surface of leather tanned using (a) control, (b) in situ-condensate melamine-formaldehyde oligomer.

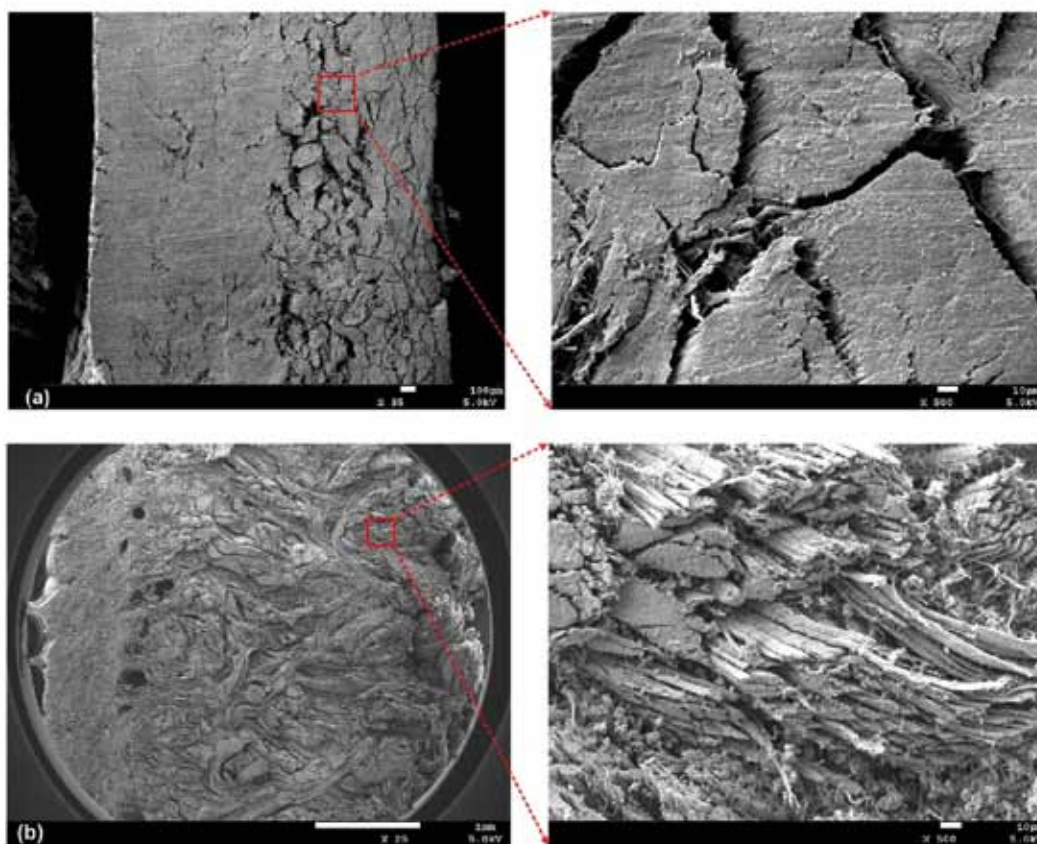


Figure 5. Scanning electron microscopic image of cross section of leather tanned using (a) control, (b) in-situ-condensated melamine-formaldehyde oligomer.

tanned leather (which usually exceeded 120°C), the hydrothermal stability is superior to the traditional melamine-formaldehyde syntan tanned one. This is because in the *in-situ* condensation process, the hydroxymethyl groups with high reactivity react with the  $-OH$  or  $-NH_2$  of collagen instead of self-condensation once they are produced, thus introducing more crosslinking between collagen chains.

#### Morphologies of Fibers in the Tanned Leather

Due to the large size caused by the self-condensation between hydroxymethyl, prepared melamine-formaldehyde syntan is often difficult to penetrate into the hides, resulting in uneven tanning or cracked grain. In the present study, an *in-situ* condensation tanning process was employed to overcome this disadvantage. Figure 4 and Figure 5 show the surface and cross section morphologies of leather tanned by *in-situ* condensate melamine-formaldehyde oligomer and control (melamine-formaldehyde syntan). It can be seen the grain surface of leather tanned with *in-situ* condensate melamine-formaldehyde is more flat and fullness without any wrinkles compared to the control sample. This should be due to the better penetrating and filling effect of the novel tanning method.

The SEM analyses of tanned leather samples showing cross section in a magnification of 350 and 500 respectively are depicted and are given in Fig. 5. The *in-situ* tanned leather shows the compactness in the fiber structure throughout the cross section and uniform structure, while the fibers seem to be less dispersed in the control sample. It is because of the better penetrating and high activity of the *in-situ* condensation melamine-formaldehyde oligomer, which opened the collagen fibers more thoroughly. Since the *in-situ* tanned leather exhibits better opened up fiber structure, it also shows increased fullness together with softness.

#### CONCLUSIONS

The present study demonstrated the feasibility of triggering *in-situ* condensation between melamine and formaldehyde monomers within bated hides to achieve a novel chromium-free tanning process, which exhibited improved tanning efficiency relative to traditional melamine-formaldehyde syntan. The multiple methylols generated from *in-situ* melamine-formaldehyde condensation can react with amino or hydroxyl groups of collagen, introducing rigid and stable chemical crosslinking between collagen chains. As a result, the hydrothermal stability of the tanned leather was

significantly improved and a higher shrinking temperature (93°C) was achieved. In addition, such *in-situ* condensation strategy can also overcome the difficulty of penetration associated with traditional melamine-formaldehyde syntan, smooth grain, more even and much looser fiber structure leather was obtained. Easy penetration, high reactivity without pickling process, high hydrothermal stability and good comprehensive properties of resultant leather revealed that the *in-situ* condensation strategy developed in this study was potential to be utilized as an alternative to chrome tannage, which eliminated the use of chromium and achieved improved tanning efficiency relative to traditional products.

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