### Synthesis of a Waterborne Melamine Resin and its Retanning Behaviors Investigation

by

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#### Abstract

Recently, the application of waterborne melamine resin (WMR) is greatly increasing in the leather industry because of its convenient operation, but it often suffers from poor storage stability. Here, two waterborne melamine resin retanning agents (WMRs) with high storage stability were prepared using melamine, glutaraldehyde and collagen hydrolysates (CHs) as raw materials at different mole ratios. FTIR, <sup>13</sup>C-NMR and XPS were used to characterize the chemical structure of synthesized resins, and their retanning behaviors for wet blue and wet white leather were fully investigated. The particle sizes of WMR1 and WMR2 were 28.73 nm and 8.78 nm, and their zeta potentials were 4.0 and 4.5, respectively. The introduction of CHs provided not only good water solubility but also amphoteric properties to synthesized resins, thereby resulting in high absorption of retanning and fatliquoring agents. Moreover, the retanning application investigation of WMRs manifested good storage stability and excellent overall performance, which are comparable with commercial retanning agents. This work showed that glutaraldehyde and CH could be used as starting materials in the synthesis of environmentally friendly WMR.

#### Introduction

Melamine-formaldehyde resin (MR) is an important retanning agent applied in the leather industry.<sup>1</sup> It is cost effective, and it shows good thickening effects when being used as a retanning agent. Recently, waterborne melamine resin (WMR) has been widely applied because of its convenient operation. However, its further application is limited because of several issues, including formaldehyde release and poor storage stability.<sup>2</sup> Although many studies have been performed in the past few years to decrease formaldehyde release in WMR, its unstable storage remains a common problem that needs effective solutions.<sup>3-7</sup>

Considering its practical relevance, several strategies have been tried to improve the storage stability of WMR. Chemically, its poor storage is due to the presence of high amounts of active methylol

groups, which will be further polymerized to large molecules and precipitated out.<sup>8,9</sup> Therefore, the common and effective approach is introducing a functional monomer to partially block some reactive groups. Methanol is usually used to react with formaldehyde and methylol melamine, which would prevent the polycondensation of methylol groups, thereby enhancing the storage stability of the final product. In addition, caprolactam and benzoguanamine are used to partly replace melamine and reduce the number of methylol groups.<sup>10,11</sup> However, although these methods can improve the storage stability of WMR, they may cause unfavorable effects to the performance of final products. In addition, sulfonation is considered as an effective way to improve the storage stability of WMR. Bisulfite can react with methylol groups, and it favors the generation of a linear polymer chain, thereby resulting in good water solubility. However, this approach may confer excessive negative charges to WMR and finally decrease the absorptance of anionic fatliquoring agents. With the development of the leather industry, a new WMR with high storage stability and good retanning performances is necessary.

Collagen hydrolysates (CHs) contain many polar groups such as amino, hydroxyl and carboxyl, and these groups result in good water solubility.<sup>12</sup> Considering that the synthesis of WMR primarily involves the reaction between the aldehyde groups of formaldehyde and the amino groups of melamine, CHs can participate in the preparation of WMR. Consequently, the polar groups in CHs can be attached to the chains of WMR, and its water solubility can be largely improved. Moreover, CHs are originated from the waste disposal of the leather industry, and they should have natural affinity with collagen fiber. These specific features can not only improve the absorption but also confer an amphoteric property to WMR.

In this paper, two WMR (noted as WMR<sub>1</sub> and WMR<sub>2</sub>) without free formaldehyde were synthesized using melamine, glutaraldehyde and CHs as raw materials at different mole ratios. The structure and retanning performances of WMRs were fully investigated.

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#### Materials and Methods

#### Materials

Analytical grade chemicals, including melamine, glutaraldehyde and triethanolamine, were all purchased from the Chengdu Kelong Reagent Chemical Factory, China. CHs (Mw≈6000) were provided by Yunnan Luliang Heping Technology Co. Ltd., China. Wet blue leather (cow hide) was obtained from a local tannery and shaved to 1.1 mm for retanning experiments. Wet white leather with 1.5 mm thickness was prepared by hydroxyl-caroxylate-Zr complex tanned cow hide. Specially, wet white leather has a higher isoelectric point than wet blue leather.

#### **Preparation of WMRs**

The preparation process of WMRs is shown in Figure 1. Before reaction, CHs were dissolved in distilled water to obtain 50 wt% aqueous solutions. The pH value of glutaraldehyde and CH was adjusted to 8.3 using triethanolamine. Then, a defined amount of melamine was added into a 500 mL three-necked glass flask equipped with a magnetic stirrer. Subsequently, glutaraldehyde solution was added to the above mentioned mixture and stirred at 65°C for 1 h to prepare the intermediates (MG). Finally, MG was added dropwise into the CH solution, and the reaction was continued for further 60 min to obtain WMRs. For the preparation of WMRs, different molar ratios of glutaraldehyde to CH were used to obtain products with different crosslinking degrees, namely, WMR<sub>1</sub> (1:3 molar ratio) and WMR<sub>2</sub> (1:6 molar ratio).

#### Characterization of WMRs

#### UV absorption spectral analysis

UV–vis absorption spectra were obtained using a spectrophotometer (Mapada UV-1800PC) with a scanning wavelength from 200 nm to 400 nm.

#### Nuclear magnetic resonance (NMR) analysis

<sup>13</sup>C-NMR spectra of melamine and MG were recorded using a Bruker AV II 400MHz NMR spectrometer (Bruker, Germany). The MG powder after lyophilization was dissolved in DMSO-D6 (30 mg/ mL). Chemical shifts were reported in parts per million (ppm) and referenced to an internal TMS standard for NMR shift control at 39.5 ppm.

#### Fourier transform infrared (FTIR) spectroscopy analysis

FTIR spectra were recorded using an FTIR spectrometer (Thermo Fisher Scientific, USA). The synthesized products were completely lyophilized using an LGJ-30F freezer dryer (XinYi, China). The powdered samples were pressed into a spectroscopic quality KBr pellet (1:200). The scanning range was 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> with 32 scans, and the spectra were presented as transmittance against wavenumber.

#### X-ray photoelectron spectroscopy (XPS) analysis

XPS elemental surface analysis was performed using an X-ray photoelectron spectrometer (Thermo Fisher Nexsa, USA) with a monochromator Al K $\alpha$  X-ray source (1486.6 eV).

#### Storage stability

The storage stabilities of obtained resins were evaluated by recording the states of solutions at 25°C during storage.

#### Particle size and zeta potential determination

Mean particle size and zeta potential ( $\zeta$ ) of WMR<sub>1</sub> and WMR<sub>2</sub> were determined using NanoBrook Omni (Brookhaven, USA). Moreover, the particle size and zeta potential of DP (amphoteric, collagen hydrolysates [CHs] contained, liquid), MRS(amphoteric, MR, liquid) and MRA (anionic, MR, solid powder) commercial retanning agents were tested for comparison.



Figure 1. Synthesis of WMRs.

Process	Chemicals	%	Duration (min)	Remarks
Rewetting	Water	400	. ,	
0	Degreasing agent	0.3	60	Drain
Washing	Water	400	10	Drain
Neutralization	Water	200		
	Sodium formate	2	30	
	Sodium bicarbonate	0.4	10	
	Sodium bicarbonate	0.4	60	pH≈5.5, Drain
Washing	Water	400	10	Drain
Retanning	Water	100	10	
	WMR <sub>1</sub> /WMR <sub>2</sub> /DP/MRS/MRA	8	90	Drain
Washing	Water	400	10	Drain
Fatliquoring	Hot water	100		
	Synthetic fatliquor	10	60	
	Formic acid	1.5	30	pH=3.8-4.0
Washing	Water	400	10	Drain, the leather was hooked to dry and staked

# Table I Retanning processes of wet blue leather

Note: based on wet white weight (w/w)

Table II           Retanning processes of wet white leather							
Rewetting	Water	400					
	Formic acid	0.3					
	Degreasing agent	0.5	40	Drain			
Washing	Water	400	10	Drain			
Neutralization	Water	200					
	Neutralization tannin	3					
	Sodium formate	2	30				
	Sodium bicarbonate	0.6*3	15*3+60	pH≈6, Drain			
Washing	Water	400	10	Drain			
Retanning	Water	100					
	Synthetic tanning agent	10	90	Drain			
	Water	100					
	WMR <sub>1</sub> /WMR <sub>2</sub> /MRS/DP/MRA	10	90	Drain			
Washing	Water	400	10	Drain			
Fatliquoring	Hot water	100					
	Synthetic fatliquor	10	60				
	Formic acid	1.5	30	pH=3.8-4.0			
Washing	Water	400	10	Drain, the leather was hooked to dry and staked			

Note: based on wet white weight (w/w)

#### **Retanning performances**

The retanning performances of WMR<sub>1</sub> and WMR<sub>2</sub> were determined, and the three commercial MR agents, namely, DP, MRS and MRA, were also tested as control samples. The wet blue leather and wet white leather were cut into halves through the backbone. The retanning processes are summarized in Table I and Table II.

#### Absorption

Absorption of retanned leather on retanning agents and fatliquors were measured on the basis of total organic carbon (TOC, Elementar, Germany) and calculated as follows:

Absorption rates = 
$$\frac{TOC_0 - TOC_1}{TOC_0}$$

where  $TOC_0$  and  $TOC_1$  were the initial TOC value and the TOC value after a particular process, respectively.

#### Physical and mechanical characteristics of leather

All samples were conditioned at 25°C  $\pm$  2°C and 65%  $\pm$  2% relative humidity for at least 48 h before testing. The mechanical strength, including tensile strength, elongation, percentage elongation at break and tear strength were measured using a universal testing machine (GOTECH, China) based on ISO 3376:2020 and ISO 3377-2:2016 approaches.<sup>13,14</sup>

#### **Results and Discussion**

#### <sup>13</sup>C NMR spectroscopy analysis

The molecular structures of melamine and MG were verified by  $^{13}$ C-NMR spectroscopy. The results are shown in Figure 2(a). The only peak in the spectrum of melamine was assigned to the triazine ring of melamine.<sup>15</sup> The spectrum of MG can be divided into three parts. The 160–170 ppm region was assigned to the triazine ring of melamine, and the region between 50 and 80 ppm was attributed to the carbon atoms in hydroxymethyl groups produced by the reaction between the -NH<sub>2</sub> group of melamine and the -CHO group of glutaraldehyde. The appearance of these peaks indicated

the successful reaction between melamine and glutaraldehyde.<sup>16</sup> In addition, the signal located at 206.64 ppm was assigned to the carbon atom that attributed to the aldehyde groups of unreacted glutaraldehyde.<sup>17</sup> This peak indicated the presence of the residing aldehyde group and provided the foundation for subsequent reaction with CHs.

#### UV absorption spectra

The UV–vis absorption spectra of CH, WMR<sub>1</sub> and WMR<sub>2</sub> are shown in Figure 2(b) to confirm the reaction between MG and CHs. Compared with CHs, a new peak was observed in WMR<sub>1</sub> and WMR<sub>2</sub>. This peak was assigned to the Schiff base originated from the reaction between the amino groups of CHs and the aldehyde groups in MG, indicating the successful reaction between MG and CHs.<sup>18</sup> Considering the results of <sup>13</sup>C-NMR and UV–vis absorption spectral analysis, we can easily conclude that melamine and CHs were successfully connected by glutaraldehyde.

#### FTIR spectroscopy analysis of MCH

FTIR spectra of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub> are shown in Figure 2(c). In the FTIR spectrum of melamine, the peak around 815 cm<sup>-1</sup> was attributed to the bending vibration of the triazine ring, and the strong peak at 1026 cm<sup>-1</sup> was assigned to -NH<sub>2</sub> swinging vibrations.<sup>19</sup> Moreover, the characteristic peaks in melamine at 3468 and 3415 cm<sup>-1</sup> corresponded to the asymmetric stretching vibrations of the -NH2 group of melamine.20 However, in the spectrum of MG, these two peaks were replaced by a broad peak at 3393 cm<sup>-1</sup>, which attributed to the tensile vibration of -OH, demonstrating the successful reaction between glutaraldehyde and melamine. Moreover, the peaks located at 2946 and 2869 cm<sup>-1</sup> of MG were assigned to the antisymmetric and symmetric vibrations of glutaraldehyde methylene, respectively, thereby reinforcing the successful reaction between glutaraldehyde and melamine. Notably, the bending vibration of C=O was observed at 1558 cm<sup>-1</sup>, indicating the presence of residue aldehyde groups.<sup>21</sup> As for WMR<sub>1</sub> and WMR<sub>2</sub>, the peaks at 1648 and 1539 cm<sup>-1</sup> were primarily assigned to amide I and amide II bands, respectively.22 These bands aroused primarily



**Figure 2.** Characterization of WMRs: (a) <sup>13</sup>C-NMR of melamine and MG, (b) UV-vis absorption spectra of CHs, WMR<sub>1</sub> and WMR<sub>2</sub>, (c) FTIR spectra of melamine, WMR<sub>1</sub> and WMR<sub>2</sub>.



Figure 3. XPS spectra of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub>.

by the reaction between aldehyde groups of MG and amine groups of CHs, indicating the successful reaction between MG and CHs.<sup>23</sup> The results of FTIR determination indicated that  $WMR_1$  and  $WMR_2$  were synthesized successfully as expected.

#### **XPS** analysis

XPS analysis of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub> was performed, and the bulk concentration of these elements is displayed in Figures 3(a)–(d). For melamine, C1s and N1s peaks were observed at 248.8 and 395.9 eV, respectively. However, MG showed an increasing intensity of O1s and a decreasing intensity of N1s, indicating the formation of covalent bonds because of the reaction between melamine and glutaraldehyde.<sup>24</sup> The XPS curve fitting data for N1s of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub> are presented in Figures 3(e)–(h). A new peak assigned to the -NH<sub>2</sub> group was observed in WMR<sub>1</sub>, which may be attributed to the residue amino groups of CHs, indicating the successful introduction of CHs.<sup>25</sup> Compared with WMR<sub>1</sub>, WMR<sub>2</sub> showed an increasing intensity of peaks for -NH<sub>2</sub>. This result was in accordance with the increasing dosage of CHs in the synthesis of WMR<sub>2</sub>. XPS analysis clearly revealed the successful reaction among melamine, glutaraldehyde and CHs.

#### Storage stability

The storage stability of WMR<sub>1</sub> and WMR<sub>2</sub> was compared with MG (Figure 4). MG, WMR<sub>1</sub> and WMR<sub>2</sub> were all obtained initially as a transparent solution. However, white precipitation was observed in the solution of MG after 1 day, whereas WMR<sub>1</sub> and WMR<sub>2</sub> still exhibited a clear and transparent solution even after 75 days. This result indicated the excellent storage stability of WMR<sub>1</sub> and WMR<sub>2</sub> and demonstrated that the introduction of CHs can improve the stability of WMRs.

#### Particle size and zeta potential

As shown in Figure 5(a), the average particle sizes of  $WMR_1$  and  $WMR_2$  were 28.73 and 8.78 nm, respectively, which were larger than that of two commercial melamine retanning agents, namely, DP (5.78 nm) and MRS (2.92 nm), but smaller than MRA (46.87 nm). These five retanning agents showed small average particle sizes, which could improve their penetration in leather.

The zeta potential of WMR<sub>1</sub>, WMR<sub>2</sub>, MRS and DP at different pH is shown in Figure 5(b). WMR<sub>1</sub>, WMR<sub>2</sub>, MRS and DP were both amphoteric electrolytes with isoelectric points at 4.0, 4.5, 4.0 and 3.2, respectively. However, MRA was anionic retanning agent. WMR<sub>2</sub> exhibited a higher isoelectric point than WMR<sub>1</sub> because WMR<sub>2</sub> conducted a high usage of CHs. Commonly, electrostatic interaction plays an important role in leather making. The increase of positive charge may pose positive effect on the absorption of subsequent



Figure 4. Storage stability of WMRs.



Figure 5. (a) Average particle size of different retanning agents. (b) Zeta potential of retanning agents at different pH.

anionic materials. Therefore, the high isoelectric points of WMR<sub>1</sub> and WMR<sub>2</sub> may improve the absorption of subsequent anionic fatliquoring agents and dyestuffs.<sup>26</sup>

## Retanning performances of WMRs Absorption

The absorption of different retanning agents and fatliquors are shown in Figure 6. Leather making is the balance between permeation and combination. Particle size and electrostatic interaction can affect the permeation and combination of chemical substances, thereby playing an important role in leather making.<sup>27</sup> As shown in Figure 6a, the absorption of all retanning agents in the retanning process of wet white leather were higher than that of wet blue leather in the same operation, which can attribute to the higher positive charge of wet white leather. MRA, an anionic retanning agent, seems to have been absorbed easily by wet white leather or wet blue leather when it applied in the retanning operation. But in fact, MRA is only partly dissolved in water, leading to the false appearance of absorption. In case of MRS, its absorption is the lowest due to its higher isoelectric point. These facts suggested that the leather with higher positive charge is favorable for the absorption of retanning agents with relative more negative change. In addition, WMR<sub>1</sub> showed a lower isoelectric point than WMR<sub>2</sub>, but it exhibited higher absorption. This result may be ascribed to the low particle size of WMR<sub>2</sub>, which is unfavorable for its combination with leather.

For the subsequent anionic fatliquors, it can be observed that the absorption of wet blue leather is higher than wet white leather due to the binding sites of wet white leather was more consumed at retanning operation, as shown in Figure 6b. This fact indicated that the retanning and fatliquoring operations should be considered together for the purpose of manufacturing good leather. In general, an amphoteric material with a high isoelectric point is favorable for the combination of subsequent anionic fatliquors. Consequently, WMR<sub>1</sub> and WMR<sub>2</sub> obtain higher results than MRS. In case of DP, its absorption is comparable with WMRs even its isoelectric point is lower than WMRs. This result may be attributed to the high affinity of CHs with collagen fibers. The collagen-based filler usually has good compatibility with collagen fibers, thereby resulting in high absorptance of retanning agents. Moreover, as shown in Figure 6(b), WMR<sub>1</sub> obtained the highest absorptance of fatliquor (91.03%), which was in accordance with the absorption of retanning agents. The high isoelectric point of WMR<sub>1</sub> is favorable for the absorption and fixation of anionic fatliquors.

#### Physical and mechanical characteristics of leather

The physical and mechanical characteristics, including tensile strength, elongation and tear strength, are all significant indicators of the durability evaluation of leather samples.<sup>28</sup> The leather samples retanned by different retanning agents are shown in Figure 7. In general, the tensile strength and tear strength of retanned wet



Figure 6. Absorption of retanned leather on retanning agents (a) and fatliquors (b).



Figure 7. Physical and mechanical properties of leather retanned by DP, MRS, WMR<sub>1</sub> and WMR<sub>2</sub>.(a) tensile strength, (b) elongation at break, (c) elongation and (d) tear strength.

white leather were higher than that of wet blue leather (Figure 7a,d), meanwhile the elongation and elongation at break were opposite (Figure 7b,c). These facts were similar with the common retanned wet white and white blue leather. The retanning effects of WMR<sub>1</sub> and WMR<sub>2</sub> were comparable with other retanning agents, but they are more convenience at application due to they are in liquid state. Specially, WMR<sub>1</sub> greatly increased the tensile strength of wet white leather, as shown in Figure 7d, probably due to its higher absorption, as shown in Figure 6a.

#### Conclusions

In this study, glutaraldehyde was conducted as a crosslinking agent to react with melamine and CHs to prepare WMRs used as retanning agents. Melamine was bonded with CHs by glutaraldehyde through the reaction between aldehydes and amino groups. Using this approach, the polar groups in CHs were attached to the chains of WMRs, and their storage stability was largely improved. Further investigation on the experimental indicated that the physical and mechanical properties of leather samples retanned by WMRs were comparable and/or even better than commercial controls. The introduction of CHs provided not only good storage stability but also amphoteric character and collagen fiber affinity to WMRs, thereby resulting in excellent retanning performances.

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