A novel preparation of formaldehyde free melamine resin and its retanning behaviors investigation

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Melamine resin (MR) retanning agent was widely used in leather industry, but often suffered the problem of formaldehyde release. Although numerous efforts have been devoted to solving the formaldehyde issue by using alternative aldehyde compounds, it often encounters a new challenge of poor storage ability due to their relative low reaction activity compared with formaldehyde. Herein, a new formaldehyde-free melamine resin MGE was prepared through a novel synthesis strategy. Melamine was firstly bonded with lysine to improve its amphoteric and water solubility, and the epoxy compound was further used as a cross-linker to prepare melamine resin. Comprehensive

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structural and performance characterization of MGE confirmed the presence of amphoteric groups in its structure. Its isoelectric point was determined to be 7.55, significantly higher than the other two commercial MR which are 2.94 and 4.69, respectively. Moreover, MGE showed high storage stability of more than six months. The physical and mechanical properties of MGE retanned leather, along with its reactivity to anionic fatliquor were also fully investigated. Owing to the ionic bonds and hydrogen bonds between MGE and collagen fibers, MGE-retanned leather showed improved physical and mechanical properties. The absorption of MGE was up to 77.08% and the thickening rate was increased by 19.23%. This study provided a new strategy to synthesis formaldehyde-free melamine resin with high stability and excellent retanning performances.

Keywords: leather, retanning agent, melamine resin, formaldehyde free, synthesis

1.Introduction

Melamine-formaldehyde resin (MR) has been widely used in leather industry for its excellent filling ability. However, the formaldehyde issue has severely hindered

its further application, because more and more stringent regulations have been established to limit formaldehyde content in leather products. Therefore, efficient alternatives are highly needed to solve the formaldehyde problem of MR(Arias, González-García, Feijoo, & Moreira, 2021; Kord, Movahedi, Adlnasab, & Ayrilmis, 2021).

Extensive works have been conducted in the past few years to address the formaldehyde problem in MR. Approaches explored by researchers can be divided into two categories(Akinyemi, Olamide, & Oluwasogo, 2019). The first one involves changing parameters in the synthesis of MR, such routes including adjusting the percentage of reactants, introducing other amino compounds, and changing the procedures of reactions in batch(J. Li & Zhang, 2021; Song et al., 2021). These methods can only reduce but not completely eliminate the formaldehyde. The second method involves using environmentally friendly reactants in the synthesis of formaldehyde-free resins, the starting compounds including glyoxal, furfural, and some natural feedstocks such as starch, tannin, and protein-based adhesives(Ji-bo, Jian-fei, Pei-lin, Xue-pin, & Bi, 2018; Kan, Sun, Kan, Bai, & Gao, 2021; Okumura, 2021; J. Wang, 2021). These synthesized MR have no aforementioned health issues, but they are mostly in the laboratory

development stage and still suffer from several obstacles such as lower reaction activity, much higher cost, or complicated synthesis procedures(Balducci et al., 2020). There still remains a great challenge to find a pragmatic pathway to realize the zero emission of formaldehyde in MR.

Glutaraldehyde is a well-known crosslinker with highly reactivity, and it is suitable to substitute formaldehyde in some regards. Regrettably, the reaction between glutaraldehyde with melamine must be sulfonation first to improve the water solubility of MR. But this process may decrease the positive charge of MR and finally influence the absorption extent of the following anionic fatliquoring agents and dyestuffs(Liu, Wang, Wang, Sun, & Wei, 2021). Therefore, the effective application of glutaraldehyde in the preparation of MR is still a challenge.

Lysine is a naturally available renewable feedstock and contains a carboxyl group and two amino groups in its molecule. The amino groups make lysine very easy to bond with melamine by glutaraldehyde. By this approach, the lysine can not only improve the water solubility but also confer amphoteric property to final MR products. Moreover, lysine supplies good compatibility with collagen fibers, thus may result in a higher absorption of synthesized retanning agents. In light of the above, it is reasonable to believe that the introduction of lysine may confer good

performances to MR.

In work described here, a new formaldehyde-free melamine resin MGE was prepared through a novel synthesis strategy. According, melamine was firstly bonded with lysine by glutaraldehyde. Then, ethylene glycol diglycidyl ether (EGDE) was further used as a cross-linker in the synthesis of formaldehyde-free MR. EGDE is one of the most important commercially compounds, it has versatile reactivity and can be severed as a substitute for the polycondensation stage to realize the crossing-linking process(Cai et al., 2021). The chemical structure of prepared MGE was characterized by FT-IR and ^{13}C-NMR, and its application properties in leather retanning process were fully investigated.

2. Materials and methods

2.1 Materials and equipments

Melamine and glutaraldehyde were analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China). Lysine and ethylene glycol diglycidyl ether (EGDE) were analytical grade and purchased from Guangdong Wengjiang Chemical Reagent Co., Ltd (Shaoguan, China). Wet blue leather (cow hide) shaved to a thickness of 1.0mm was obtained from a local tannery.

2.2 Preparation of MGE

Aqueous solution of glutaraldehyde (50% by weight) was used in this study and MGE was prepared as following steps. First, pH value of the glutaraldehyde solution was maintained to 8.0–8.5 by using 1 M NaOH solution and taken into a 250 mL three-necked flask equipped with magnetic stirrer. The reaction bath was kept at 60°C. A definite mole proportion of melamine was then added to the flask and stirred until melamine is completely dissolved. This process was recognized by the color change from a white suspension to a clear solution and the intermediate products was named MG. After that, lysine was dissolved by an equal mass of water and added to the system. The reaction was continued for further 30 min after the addition of lysine and the intermediate product of this procedure was named MGY. Then, the pH of MGY was adjusted to 5.0 by using 1 M HCl solution and different rations of EDGE (1%, 2.5% and 5% based on total weight of MGY, respectively) were added dropwise with vigorous stirring and kept for 120 min, the products were named MGE1, MGE2 and MGE3, respectively. Finally, the clear solution was cooled down naturally and MGE was obtained. The synthetic scheme was illustrated in Figure 1.

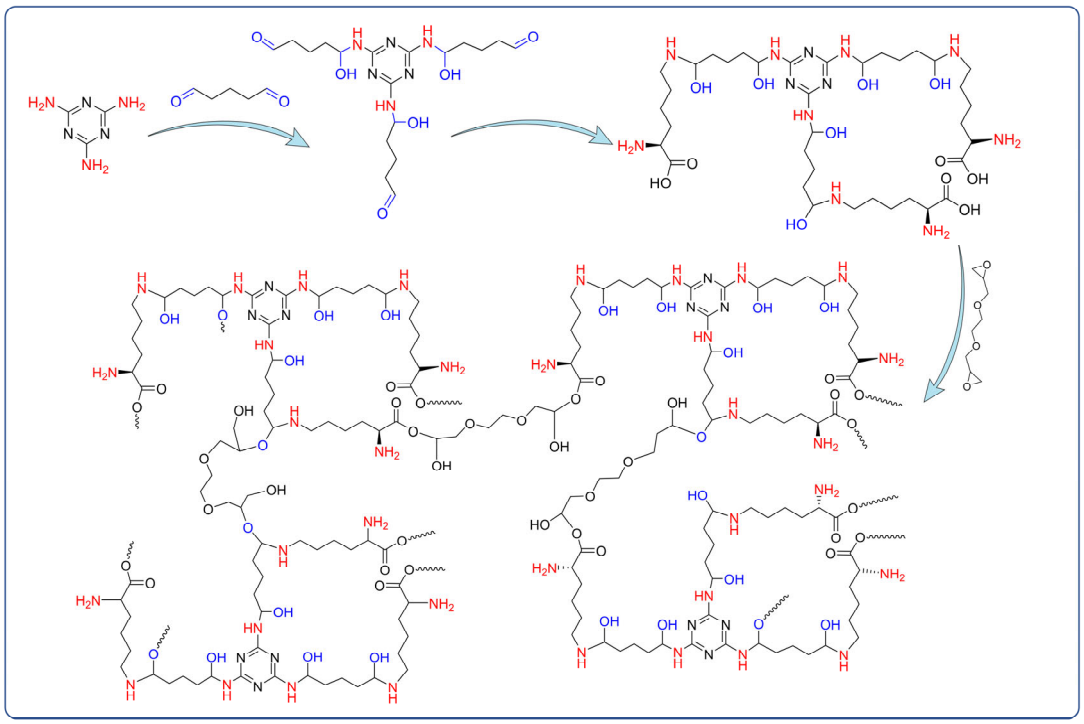

Figure 1. The schematic representation of MGE preparation processes

2.3 Characterization

2.3.1 FT-IR Analysis

The FT-IR spectra of melamine, MG, MGY and MGE were performed in a Nicolet IS10 (Thermo Scientific, USA) spectrometer. The test was carried out using compressed pellets of KBr and the wavenumber range from 400 to 4000 cm^{-1}.

2.3.2 Nuclear magnetic resonance spectrum (^{13}C-NMR)

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 400MHz NMR spectrometer (Bruker, Swiss). The solvent was heavy water (D_2O).

2.3.3 Particle size and isoelectric point (pI) analysis.

The average particle size and the zeta potential measurements were determined by NanoBrook Omni (Brookhaven, USA). Samples were dissolved in water to a final concentration of 1g/L and their pH were adjusted 2-10 with 1mol/L HCl and 1mol/L NaOH to further determine the isoelectric point (pI). Two commercial amino resin retanning agents named CMS and CML were used as control samples.

2.4 Application performances test

For this study, the wet-blue (chrome tanned) was used as raw materials to evaluate the application performances of prepared MGE. The leather samples were cut into two halves through the backbone and divided into 30 × 30 cm, their thicknesses were about 1.2 mm. Moreover, two commercial amino resin retanning agents named CMS and CML were used as control. The application processes were summarized in Table 1.

Table 1 Retanning Processes

Process	Chemicals	%	Duration(min)	Remarks
Rewetting	Water	400		
	Degreasing agent	0.3	60	Drained
Washing	Water	400	10	Drained
Neutralization	Water	200		
	Sodium formate	2	30	
	Sodium bicarbonate	0.4	10	
	Sodium bicarbonate	0.4	60	
Washing	Water	400	10	Drained
Retanning	Water	100		
	CMS/CML/MGE	8	60	
Fatliquoring	Synthetic fatliquor	10	30	
	Hot water	100	30	
	Formic acid	1.5	30	Drained
Washing	Water	400	10	Drained. The leather was hooked to dry ad staked

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

2.4.1 Absorption of the retanning agents.

The content of retanning agents in waste water before and after retanning process were determined by gravimetric method (Shi et al., 2013). The absorption of retanning agents were calculated according to equation (1).

$$\text{Absorption of retanning agents} = \frac{A_1 - A_2}{A_1} \qquad (1)$$

Where A_1 is the content of retanning agents in initial liquid and A_2 is the content of retanning agents in liquid after retanning process was completed.

2.4.2 Determination of the absorbance of fatliquoring agent.

In order to explore the effects of the MGE on the absorption of anionic fatliquoring agents, the absorbance of fatliquoring agents were calculated respectively in this experiment according to referenced methods. First, the fatliquoring liquids in initial and finished fatliquoring aqueous solutions were gathered alone, and the fatliquoring contents were tested by TOC. Then, the absorbance of fatliquoring agents were calculated by formula (2).

$$\text{Absorption of fatliquoring} = \frac{B_1 - B_2}{B_1} \qquad (2)$$

Where B_1 and B_2 are the contents of fatliquoring in the beginning and finished fatliquoring liquids, respectively.

2.4.3 Determination of the physical and mechanical properties of leathers.

The physical and mechanical properties of leather samples, such as tensile strength, tearing strength were tested by an electronic universal testing machine as per the standard IULTCS(JMV Williams, 2000; J Williams, 2000).

2.4.4 Softness and fullness of leather

The softness of leather samples were measured using a standard method, and their fullness were evaluated by measuring the compressed and resilient thicknesses of leathers according to the method described in literatures(36, 2000; Ding, Yi, Wang, Zhou, & Shi, 2018). In general, higher compressed and resilient thicknesses mean better fullness.

3.Results and discussion

3.1 FT-IR and ^{13}C-NMR of synthesized resin

The chemical structures of melamine (ME), MG and MGE were all characterized by FTIR, as shown in Fig. 2a. The spectrum of ME was observed four characteristic absorption peaks at 3468, 3418, 3332 and 3131 cm^{-1}, which belonged to the stretching vibration absorption of $-NH_2$ groups(Zhu et al., 2020). After the reaction of melamine and glutaraldehyde, the peaks of $-NH_2$ were replaced by a

broad absorption peak at 3444 cm^{-1} in the spectrum of MG. This peak was assigned to the stretching vibration of hydroxy groups, proves the successful reaction of melamine and glutaraldehyde(C. Wang, Wu, Li, Mu, & Lin, 2020). The presence of residue aldehyde groups can be confirmed by the peak at 1566cm^{-1}, these aldehydes provide the foundation for subsequent reaction with lysine(Salmani, Abedi, Mozaffari, & Sadeghian, 2017). Additionally, MG exhibited a new absorption peak at 997 cm^{-1} compared with melamine, this peak may attribute to the hydrate of glutaraldehyde. In the FTIR spectrum of MGY, the peak at 997 cm^{-1} disappeared and a new peak at 1625 cm^{-1} assigned to the N–H bending vibration was observed after the addition of lysine, proves the successful reaction between hydroxy and amino groups. After the addition of EDGE, the characteristic peak of epoxide groups at 907 cm^{-1} was almost disappeared and the vibration of ether bond C–O–C at 1179 cm^{-1} and 1051 cm^{-1} were observed, confirming the successful reaction of epoxide groups(Gargol, Klepka, Klapiszewski, & Podkościelna, 2021). Moreover, a characteristic absorption peak of ester groups was observed at 1786 cm^{-1}, implies the reaction between epoxide groups and carboxyl. According to above analysis it is reasonable to believe that melamine, glutaraldehyde, lysine and EDGE have successfully reacted.

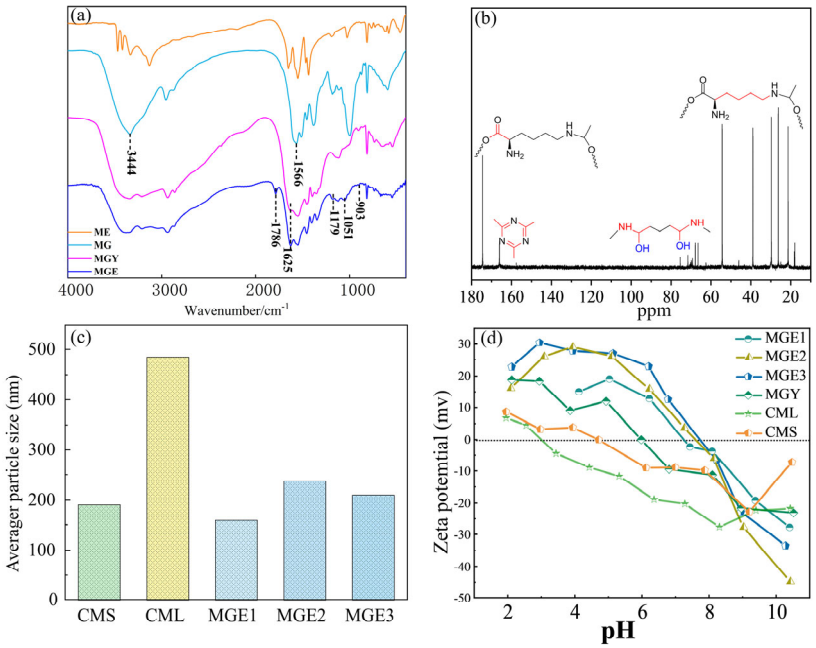

Fig. 2. Characterization of MGE (a) The FT-IR spectra. (b) ^{13}C-NMR of MGE. (c) The average particle size. (d) Zeta potential

The chemical structure of MGE was further characterized by ^{13}C-NMR spectroscopy, as offered in Fig. 2b. First of all, the peak of unreacted melamine at 173 ppm was not observed and the signal observed at 166.1 ppm was assigned to the substituted melamine triazine carbons, indicating the fully reaction of melamine(Deng et al., 2018; Mao, Hassan, & Kim, 2013). Similarly, the absence of the peak at 206 ppm for the carbon of unreacted aldehyde groups in MG also reflects the successful reaction between MG and lysine(No & Kim, 2004). Additionally, the successful introduction of lysine can also be confirmed by the

peaks at 17.98-54.37 ppm region, these peaks are attributed to different lysine residues(Eggen & Glomb, 2021; Zhang et al., 2020). Moreover, the 60-80 ppm region were assigned to carbons that linked with the reactions of hydroxyls, these reactions contain the condensation of hydroxyls and the ring-opening reaction between hydroxyls and epoxy groups(Z. Li et al., 2021). Specially, the peak at 62.5 ppm and 69.87 ppm were attributed to the carbon that linked to the ring-opening of epoxy groups and the aliphatic ether bonds of EDGE, respectively. According to literatures, the peak of ether bonds originated from the condensation of hydroxyls should be located at 80-90 ppm, it is notable that this peak was missing in the spectra of MGE, indicating the suppression of methylene-ethers(No & Kim, 2004). Furthermore, the reaction of carboxyl and epoxy group is reinforced by the presence of peak at 174.5 ppm, this peak was assigned to esters generated from the reaction of carboxyl and epoxy groups(Abd-El-Aziz, El-Ghezlani, & Abdelghani, 2020). The higher intensity of this peak suggests that the crosslinking mainly took place between carboxyl and epoxy groups.

3.2 Average particle sizes and zeta potential

The average particle sizes of different resins were determined by Zetatrac particle

size analyzer and shown in Fig. 2c. It can be seen that CML exhibited the largest average particle size of 483 nm and the other four resins showed similar average particle sizes of 150-224 nm. Commonly, small particles can easily permeate and further combine with collagen fibers in leather making process. Moreover, benefit from the introduction of lysine, MGE carries abundant functional groups on its main chains. It is advantageous for MGE to form a multi-points interaction with collagen fibers. From the results of particle size testing, it is reasonable to believe that MGE may show good permeability properties in retanning process.

Additionally, electrostatic interaction was viewed as one of the most important reaction types in leather making process. The charge properties of melamine resins at different pH were further analyzed. As can be obviously seen from Fig. 2d, the zeta potential of MGE increased progressively with the increasing dosage of EDGE. Combined with the 13C-NMR analysis results, it can be concluded that the consumption of carboxyl lead to the decreasing of negative charge and finally result in the increase of zeta potential. Moreover, as shown in Fig. 2d, the isoelectric point of MGE3 is 7.55, obviously higher than that of the other two commercial amino resins which are 2.94 and 4.69. Lysine is an alkaline amino acid, and there are large amount of nitrogen atoms served as positive charge centers in

the reaction system(Ahmad, Ahmad Kamarudin, Leow, & Rahman, 2020). Moreover, different from traditional synthesis of MR, the sulfonation reaction process was replaced by the introduction of lysine in the preparation process of MGE, resulting the greatly reduction of negative charge centers(X. Wang et al., 2021). In addition, the carboxyl groups will be consumed by the reaction with epoxy groups, the pI of MGE will be inevitably increased. The higher pI is important in leather retanning process, it can improve the binding rates of subsequent anionic fatliquoring agents.

3.3 Retanning behaviors of MGE

3.3.1 Absorptivity of MGE and fatliquoring agents

Fig. 3a shows the absorption rates of leather samples retanned by different melamine resins. It can be obvious seen that the absorption of MGE was up to 77.08%, significantly higher than that of the other resins. It could be suggested that the introduction of lysine in MGE established a biomimetic structure to collagen, which prompt it easily diffuse into collagen fiber system. Moreover, the smaller particle size of MGE also created a favorable condition for its penetration in leather. Additionally, MGE contained abundant functional groups such as hydroxyl, amino

and carboxyl, these groups are involved in the formation of interaction among MGE, Cr^{3+} and leather fibers. Ultimately, the strong bond capacity and penetration ability lead to a higher absorption of MGE.

Fig. 3b illustrated the absorption rates of fatliquoring agents. It can be seen that leather retanned by MGE also showed a higher absorption rate of fatliquoring agents than others. As we know, the introduction of amphoteric polymers into retanning process will facilitate the absorption and binding of subsequent materials through the regulation of charge(Hao et al., 2020). As mentioned above, MGE was amphoteric and showed a higher pI, these features can improve its binding ability with collagen fiber and anionic materials, which ultimately leading a higher absorption rate of anionic fatliquoring agents.

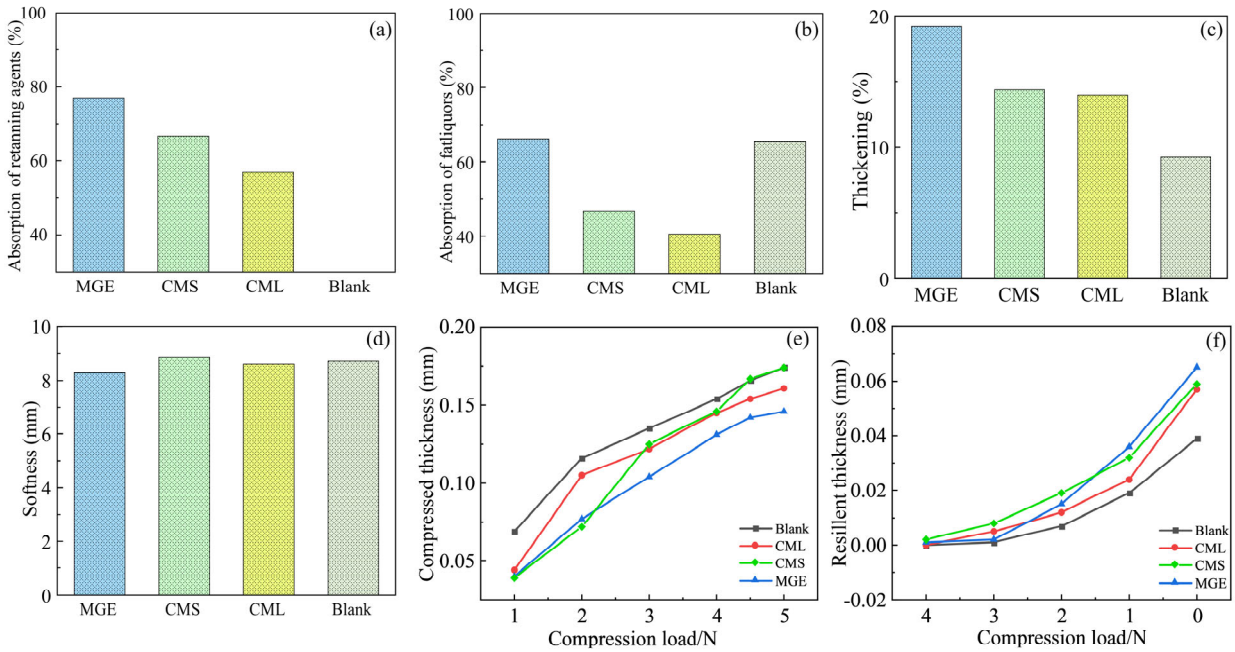

Fig. 3 (a) Absorption of retanning agents. (b) Absorption of fatliquoring agents. (c)Thickening rate. (e)the softness of different leather samples. (f)the fullness of different leather samples

3.3.2 Thickening rates

Thickening rate is an important index to evaluate the performance of melamine resins. Fig. 3c shows the thickening rates of leather retanned by different melamine resins. As illustrated, leather retanned by MGE showed the highest thickening rates of 19.23%, indicating its excellent retanning performance.

3.3.3 The softness and fullness of leather

Fig. 3d shows the softness of different leather samples. It can be seen that the softness of MGE retanned leather decreased to 8.28 mm compared to the blank

(8.7 mm). This result suggested that MGE retanned leather decreased the lubricating degree of collagen fibers, confirming that MGE can endowed leather with higher internal crosslinking intensity(Ding et al., 2020).

Fig. 3e and Fig. 3f shows the fullness of different leather samples. As can be seen, MGE retanned leather showed a better fullness than CMS and CML. This may be attributed to two effects: (1) MGE contains abundant functional groups, these groups make it more effectively to be interlocked in the structures of collagen fibers, thus showed a satisfactory fullness behavior. (2) MGE shows an amphoteric property, it can facilitate the absorption and binding of anionic fatliquors through the regulation of charge, thus leading to a better performance of leather(Hao et al., 2020).

3.3.4 Chromium discharge in effluent

As we know, the chromium that combined with collagen can be released from crust leather in the subsequent processes such as retanning, dyeing, fatliquoring, and so on(Lyu, Chang, Gao, & Ma, 2018). The concentration of chromium in effluents were measured by ICP-AES to evaluate the effects of different melamine resins on the release of chromium, as shown in Fig. 4a. It can be observed that MGE retanned leather showed an obvious lower release of chromium than others. This

may attribute to the abundant functional groups of MGE, which can chelate with chromium.

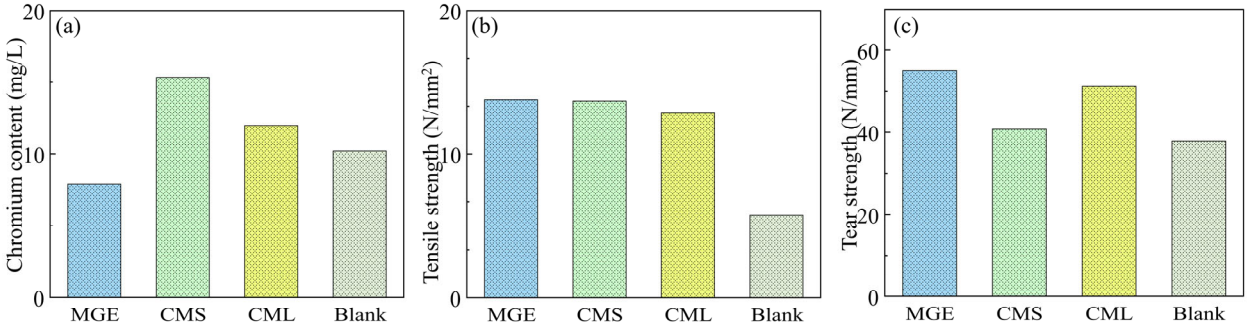

Fig. 4 (a) Chromium discharge in effluents. (b) Tensile strength of leather samples. (c)Tear strength of leather samples

3.3.5 Physical and mechanical properties

Tensile and tear strength tests were carried out for all samples and the results were presented in Fig. 4b and 4c. As can be seen, MGE, CMS and CML showed a similar tensile strength and MGE exhibited obvious higher tear strength. Combined with absorption and thickening results, this result also indicates that MGE can form a multi-points cross-linking structure with collagen fibers. Generally speaking, hydroxyl, carboxyl and amino groups in MGE are all helpful in the interaction with chromium tanned collagen fibers(Lyu, Wang, Ma, Gao, & Jin, 2016). These groups can form hydrogen and coordination bonds with collagen and

chromium ions, thus improving the mechanical strength.

4. Conclusion

In this study, melamine was firstly bonded with lysine to improve its amphoteric and water solubility, and a novel formaldehyde-free melamine resin MGE was prepared by epoxy cross-linking strategy. Due to the introduction of lysine, MGE showed an amphoteric property and a high storage stability. Because of the amphoteric property and abundant functional groups, MGE can facilitate the absorption of fatliquoring agents and reduce the release of chromium. These results revealed that the epoxy cross-linking strategy could be a potential alternative for the synthesis of formaldehyde-free melamine resin.

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