

Preparation of Formaldehyde-free Melamine Resin using Furfural as Condensation Agent and its Retanning Performances Investigation

by

Zhou Ji-bo,^a Li Pei-lin,^a Zhou Jian-fei,^a Liao Xue-pin^{a,b} and Shi Bi^{a,b}

^a*Department of Biomass and Leather Engineering, Sichuan University*
Chengdu 610065

^b*National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University,*
Chengdu 610065

Abstract

Amino resins are one of the most important retanning agents used in the leather industry. However, the generally presence of formaldehyde greatly restricts the widespread application of amino resins. In this study, furfural, an organic compound derived from biomass material, was used to substitute for formaldehyde in the synthesis of melamine resin based on an alkaline-acid procedure. The as-synthesized formaldehyde-free melamine resin (MRf) showed excellent performances in leather processing. FTIR and ¹³C-NMR were used to characterize the chemical structure of MRf. The particle size as well as zeta potential were also determined. The retanning performances of MRf indicated that the overall performances of MRf are comparable to conventional formaldehyde contained melamine resin (MR) and commercial melamine resin (CMR). In particular, the thickness of the leather retanned by MRf was enhanced around 10.33%, which is significantly higher than that of controls MR (6.16%) and CMR (5.94%). Color measurements showed that MRf imparted leather with higher dark intensity. This present work demonstrated that furfural could be a potential candidate to replace formaldehyde in the production of formaldehyde-free melamine resin.

Introduction

Amino resins (AR) are one of the most important retanning agents used in the leather industry, due to their outstanding advantages, especially imparting excellent physical and organoleptic properties to leathers.¹ However, most amino resins are synthesized based on the condensation of formaldehyde with amino compounds like urea, dicyandiamide, and melamine. Thus, the emission of formaldehyde from leather products is inevitable, due to the release of uncondensed formaldehyde and the splitting of ether bridges or terminal hydroxymethyl groups.²

As a known carcinogen, the use of formaldehyde has posed dissatisfaction and health related complaints among global consumers.³⁻⁶ Moreover, the application of formaldehyde has been restricted by International Agency Research on Cancer (IARC) for its possible harmful side effects of nose and throat cancer in humans.⁷ Therefore, it is an important concern to reduce or even completely eliminate formaldehyde emission in the residual composition with AR and related leather products.

Changing the molar ratio of formaldehyde to melamine in the preparation of resin has been recognized as one of the most economical methods to decrease the free formaldehyde content. However, this method usually adversely affects the physical and organoleptic properties of the leather products.⁸ The introduction of formaldehyde scavengers may lead to the lower concentration of formaldehyde, sometimes achieving an allowable limit, but without certainty. Urea, trolamine, sodium metabisulfite, dicyandiamide, and many other chemical additives have been tried under that guideline.⁹⁻¹⁰ Likewise, it was reported that grape seeds in all forms used in retanning process can lower free formaldehyde content.¹¹ However, the costs and properties of final leather may be seriously affected if high amounts of chemical additives are applied.

The most recognized effective route is to look for a non-toxic aldehyde as incorporating monomer alternatives, while the performance of the suitable alternative synthesized resin should meet the requirements for leather. Namely, it should be comparable with formaldehyde-based amino resins in leather industry. Much previous work has replaced formaldehyde by natural products derived from sodium alginate.¹² Glyoxal has also been used as condensing agent to produce a formaldehyde-free retanning agent.¹³

Furfural, also named as furan, is originated from natural biomass and may be considered as a "green" condensation agent.

*Corresponding author e-mail address: xpliao@scu.edu.cn, cell phone: +8613060063330

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Furfural polycondensate is of great interest of both fundamental and industrial research.¹⁴ Furfural can be obtained by acid dehydration of polymeric pentose from renewable sources, such as corncobs, oat meal and wheat bran.¹⁵ It has been recognized as one of the most promising high value-added platform chemicals, and therefore the use of furfural appears to be one of the most attractive and promising options for achieving environmental friendly and sustainable production of chemicals.¹⁶

Due to the chemical properties of furfural allowing the typical reactions of aldehyde, it could be used in the synthesis of amino resins as an aldehydic copolymer component.¹⁷ Several studies have been conducted to investigate the possibility of furfural applied in wood-adhesive formulation.¹⁸⁻²¹ However, the chemical reaction behaviors of furfural are very different compared to aliphatic aldehydes. It was found that polymer precipitation was produced when formaldehyde was substituted with furfural in the preparation process of AR.²² Therefore, the effective application of furfural in the preparation of AR remained challenging.

Melamine resin (MR) is categorized as one type of AR, and it has been generally prepared by the reactions of melamine and formaldehyde. Therefore, the emission of formaldehyde is also the main problem of MR. In this study, an attempt was made to investigate the possibility of using the biomass-derived furfural as alternative to formaldehyde in the synthesis of MR, so that a formaldehyde-free and environmental friendly retanning agent (MRf) preparation process can be developed. Considering the rigid ring in the structure of furfural, the filling behaviors of as prepared MRf should be improved over that of common MR. Chemical structure of MRf was characterized by using Fourier transform infrared spectroscopy (FTIR) and ¹³C magnetic resonance spectroscopy (¹³C-NMR), and its retanning behaviors were further investigated.

Materials and Methods

Materials

Analytical grade chemicals, including melamine, furfural, formaldehyde, methyl alcohol, sodium hydrogen sulfite, and other chemicals were purchased from Chengdu Kelong Reagent Chemical Factory, China. CMR, used as comparison, is a solid commercial product of MR and supplied by Decision Chemicals Co. Ltd., China. Wet blue leather (cow hide) was obtained from a local tannery and shaved to 1.0mm in thickness for retanning experiments.

Preparation of MRf Resin

The MRf was synthesized by a typical alkaline-acid procedure. First, defined amount of furfural, melamine and distilled water were introduced into a 500ml three-necked glass flask equipped

with a thermometer, reflux condenser, and mechanical stirrer. Before reaction, pH value of the mixture was adjusted to ~9.0 with NaOH solution (0.1 M), followed by increasing the temperature to 80°C under reflux for 1h. Subsequently, NaHSO₃ was added to the flask and the pH was adjusted to ~10.0 to begin sulfonation reaction. 2 h later, methyl alcohol was then introduced, and the pH of system was adjusted 4.5-5.0 using hydrochloric acid (0.1 M) and held for 0.5h to further complete blocking reaction. Finally, the reaction system was cooled down to ambient temperature, and a transparent MRf was obtained. Also, a formaldehyde-based melamine resin (named as MR) was synthesized as the same method of MRf. Solid contents of MRf and MR were determined by heating 10g of each sample in an aluminum pan and placed in a convective oven at 105°C for 3hr until constant mass.

Characterization of MRf

Fourier Transform Infrared(FTIR) Spectroscopy Analysis

FTIR studies were performed in a FT-IR spectrometer (Thermo Fisher Scientific, USA). KBr folium samples with a mass of about 1/100 were produced. Spectrum was recorded in the range of 4000-500 cm⁻¹ by signal averaging of 32 scans at a resolution of 4 cm⁻¹. The spectra were recorded as percentage transmittance versus wavenumber.

Nuclear Magnetic Resonance (NMR) Analysis

The liquid ¹³C NMR spectrum of the MRf was obtained on a Bruker AV II 400MHz NMR spectrometer (Bruker, Germany). The liquid MRf was lyophilized using LGJ-30F freezer dryer (XinYi, China) and then dissolved in deuterated dimethyl sulfur oxide (DMSO-D₆). The chemical shifts were referenced to TMS((CH₃)₄Si) dissolved in DMSO for NMR shift control at 39.5 ppm.

Particle Size and Zeta Potential Determination

The average particle size and size distribution, as well as zeta potential of MRf at different pH were determined using NanoBrook Omni (Brookhaven, USA). For further comparison, the zeta potential of MR and CMR were also tested, respectively.

Retanning Performances of MRf

Retanning experiments were carried out to evaluate the application performance of MRf. The synthesized MR and a commercial CMR (formaldehyde containing) were also tested for performance comparison. The retanning processes were summarized in Table I.

Table I
Retanning processes.

Process	Chemicals	%	Duration(min)	Remarks
Rewetting	Water	400		
	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	
Washing	Water	400	10	Drain
Retanning	Water	100		
	MRf/MR/CMR	8	30	
Dyeing	Acid dye (Dark)	2	60	
Fatliquoring	Synthetic fatliquor	10	30	
	Hot water	100	30	
	Formic acid	1.5	30	Drain
Washing	Water	400	10	Drain. The leather was hooked to dry and staked

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

Physical and Mechanical Characteristic of Leather

Samples for testing were obtained according to the standard method from leathers both along and across backbone line. Specimens were conditioned at 25±2°C and 65±2% relative humidity over a period of 48 hours before test.²³ The mechanical strength including tensile strength, elongation, percentage elongation at break and tear strength were examined with a universal testing machine (GOTECH, China) according ISO 3376-2011 and ISO 3377-2016 approaches.²⁴⁻²⁵

The thickness of crust leathers was measured with a dial thickness gauge (MingYu, China), and the thickening percentage was calculated as follows:

$$\text{thickening percentage}(\%) = \frac{TH_a - TH_b}{TH_b}$$

Where, TH_b and TH_a are the average thickness of nine different points of leather measured by gauge before and after retanning, respectively.

The softness of leather was measured with a ball pressure softness tester (GOTECH, China). The shrinkage temperature of leather in glycerol medium was measured using shrinkage temperature meter.

Color Measurements

Color measurement parameters such as L , a and b were recorded using a CR-13 color reader instrument for leathers retanned by MRf, MR and CMR, respectively. A dyeing leather sample without retanning was recorded as reference. " L ", " a " and " b " represent lightness, red and green axis, yellow and blue axis, respectively. The total color difference ΔE were calculated as following:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

Where ΔL , Δa and Δb are the difference in L , a and b , respectively. ΔL , Δa and Δb were calculated by subtracting the corresponding value from reference.

Analysis of Free Formaldehyde Content in Leather

Samples from experiments and control leathers were analyzed for free formaldehyde using the standard ISO/TS 17226-2008 approach.²⁶ Initially, a 0.1% solution of sodium dodecyl sulphonate was used to extract the formaldehyde in leather by gentle shaking at 40°C for 30 ± 2 min. Then, a glass fiber filter was used to filter the extract solution, and an aliquot of the filtrate is reacted with dinitrophenylhydrazine for 60 min. Finally, the content of formaldehyde is determined by HPLC (Agilent, USA) using a Zorbax Ecilepse XDB-C 18 column (4.6 mm × 250 mm 5µm) with the absorbance measured by a diode array detector at 412nm.

Results and Discussion

Preparation of MRf

Generally, the water solubility of melamine is very limited, but it can be solubilized along with the reaction process when formaldehyde is employed.¹³ However, water insoluble precipitate was obtained when furfural was used in the preparation of MRf due to its limited water solubility. Thus, the sulfonation reaction should be introduced after furan-hydroxylation reaction to get water soluble MRf. Meanwhile, considering the fact that high temperature may result in oxidation of furfural, the reaction temperature was conducted at around 80°C. The solid content of MRf and MR were 46.01% and 41.27%, respectively.

FTIR Spectroscopy Analysis of MRf Resin

FTIR spectra of MRf and melamine were presented in Figure 1. In case of melamine, absorbance peaks located at 3468cm⁻¹ and 3417cm⁻¹ are corresponded to the asymmetric stretching vibrations of -NH₂ group of melamine.²⁷ However, in case of MRf, these two peaks disappeared, indicating the reaction between the -NH₂ group of melamine and the -CHO group of furfural proceeded. Furthermore, there occurs a new broad peak at 3352cm⁻¹ which indicated that a lot of -OHs were formed.²⁸ The C-N asymmetric stretching of amides is revealed by the vibration at 1552cm⁻¹.²⁹ The appearance of peak at 930cm⁻¹ could be ascribed to the C-H deforming vibrations in the furan ring of furfural, while the peak at 590 cm⁻¹ should be the in-plane ring breath of the entire furan ring.³⁰ These facts suggested that furfural has successfully incorporated with melamine. This conclusion is further supported by C=C stretching vibration of furan rings which is observed at 1498 cm⁻¹.³¹ The peak at 2967 cm⁻¹ is prominently due to the C-H stretching vibration.³² The C-O-C stretching can be observed at 1211cm⁻¹, further providing strong evidence for the formation of a methylene bridge. The peak at 1046 cm⁻¹ corresponds to the characteristic asymmetric stretching of sulfonic group, this substantiates the successful

proceeding of the sulfonation reaction.³³ Moreover, bending vibration of triazine ring was found at 814 cm⁻¹.³⁴ In summary, furfural was reacted with melamine and the sulfonation reaction was successful.

¹³C NMR Spectroscopy Analysis

The molecular structure of MRf was further verified by ¹³C NMR spectroscopy and the result was showed in Figure 2. The definition and allocation of carbon groups were determined according to the references.³⁵⁻³⁸

As shown in Figure 2, the spectrum of MRf can be divided into three parts. The 160 to 170 ppm region could be assigned to the aromatic rings of the triazine. The region between 100 and 150

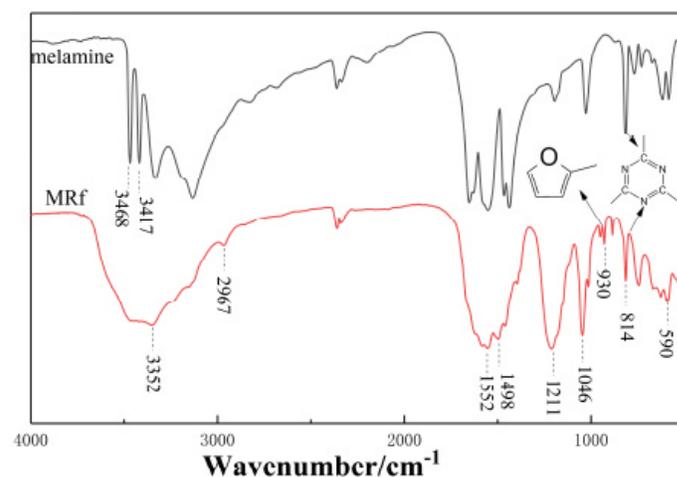


Figure 1. The FT-IR spectra of melamine and MRf.

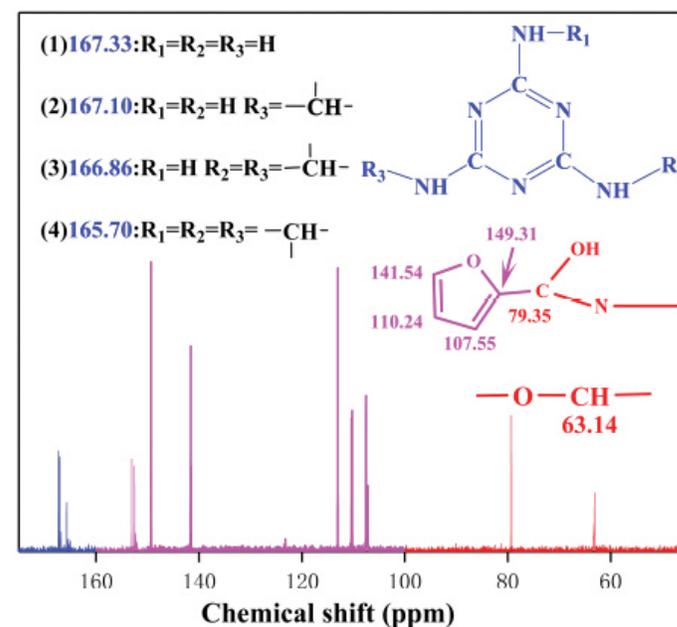


Figure 2. ¹³C-NMR spectra of MRf.

ppm attributed to the carbons present in the furan ring and region between 60 and 80 ppm to carbon atoms present in methine units derived from the reaction between the $-NH_2$ group of melamine and the $-CHO$ group of furfural.

In the triazine ring region, the carbons in the melamine ring appeared at 167.33, 167.10, 166.86, and 165.70 ppm, which corresponding to unreacted, monosubstituted, disubstituted and trisubstituted melamine, respectively, as shown in legend (1) ~ (4) of Figure 2.

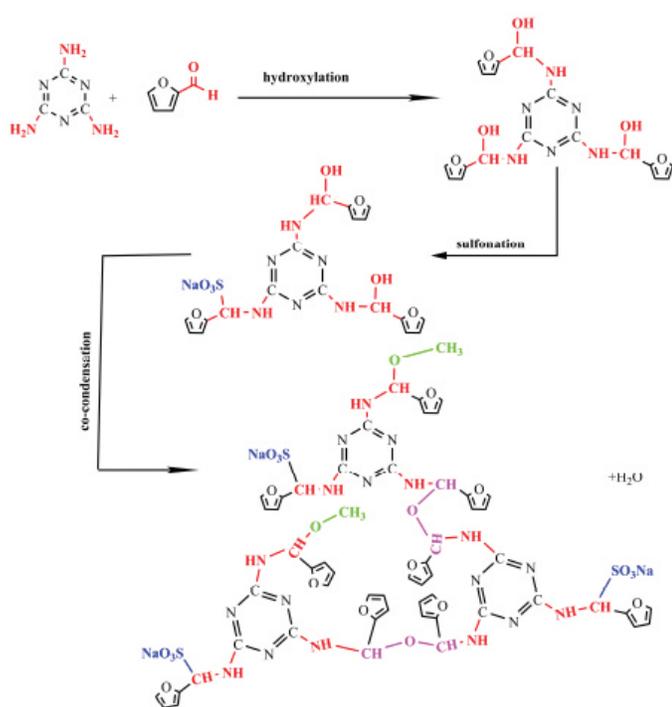


Figure 3. Possible reaction process for the preparation of MRf.

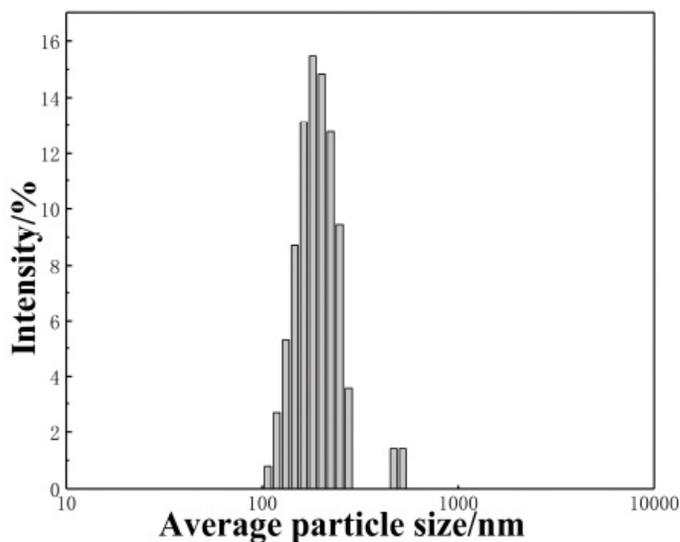


Figure 4. Particle size and distribution of MRf.

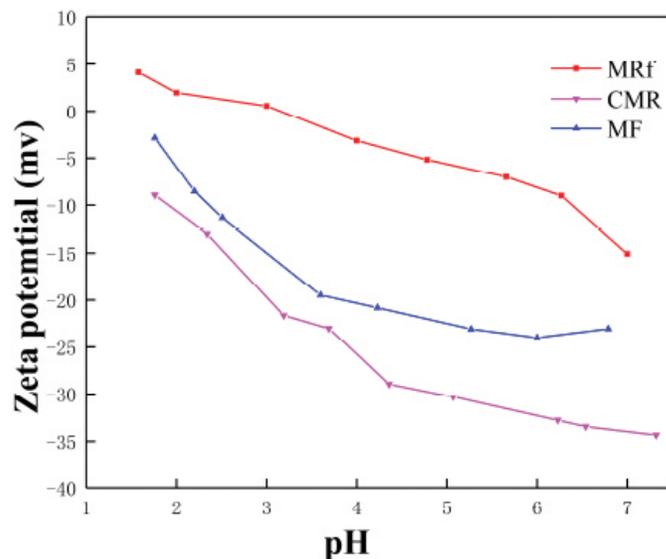


Figure 5. Zeta potential of retanning agents at different pH.

Table II
Physical and mechanical properties of the leathers retanned with MRE, MR, and CMR.

	MRf		MR		CMR	
	along	across	along	across	along	across
Tensile strength, N/mm ²	31.11	27.93	25.43	25.00	31.43	27.66
Elongation, 10N/mm ²	24.56	24.39	28.48	27.99	27.17	28.03
Elongation at break, %	48.06	49.99	47.07	50.64	51.92	53.27
Tear strength, N/mm	116.44	102.97	81.02	78.31	91.12	82.25

Four distinguished peaks at 107.55 ppm, 110.24 ppm, 141.54 ppm and 152.51 ppm could be assigned to the four characteristic C atoms on the furan ring. The peak at 79.35 was attributed to the carbons of methine units, verifying the reaction between $-NH_2$ group and $-CHO$ group. In addition, $-O-CH-$ ether carbons appeared at 63.14ppm further confirming the blocking reaction of methyl alcohol.

In summary, the analysis results of FTIR and ^{13}C NMR spectroscopy verified the successfully reaction between melamine and furfural, corresponded with the sulfonation and blocking reaction. The possible reaction process for the preparation of MRf was presented in Figure3.

Particle Size and Zeta Potential

Leather manufacture is mainly a process involving penetration, distribution and fixation of chemicals in the leather matrix.³⁹ Penetration and distribution of the retanning agents in the leather matrix are influenced by colloidal particle size and surface charge of the substrate. The average particle size and distribution of 10% wt MRf are shown in Figure 4. It can be seen that the particles are distributed in a range mainly between 100 to 248 nm. The average particle size of MRf is 209.96 nm with polydispersity coefficient (PDI) 0.157, indicating a wide distribution of particle size. It was reported that the constrict pore diameter of wet-blue leather is around 1000 nm. Thus, the as prepared MRf can well permeate into the inside of leather in the retanning process and further interact with collagen fibers to fill up the fibril gaps.⁴⁰ Furthermore, the two rigid rings (triazine and furan ring) existed in MRf could bring positive effects to the thickness of retanned leather.

The surface charges of MRf, MR, and CMR at different pH are shown in Figure 5. MRf is an ampholyte so its isoelectric point is about 3.0. However, MR and CMR are all negative charged. In

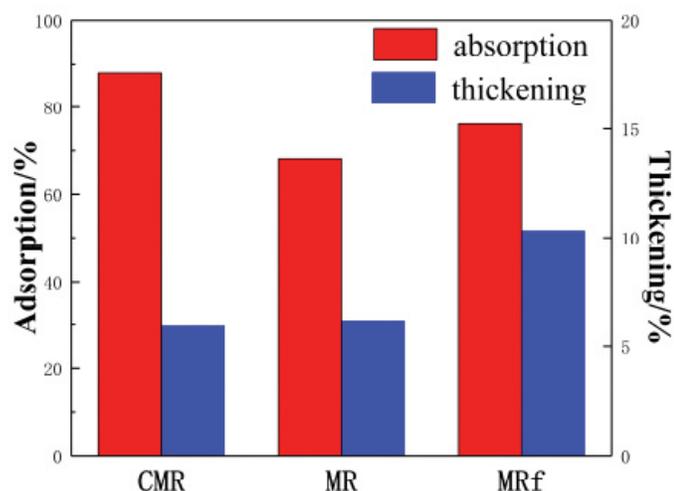


Figure 6. Adsorption and thickening of leather retanned by CMR, MR and MRf.

the synthesis of MRf resin, furfural undergoes an addition reaction with amino group of melamine with the formation of substituted melamine. However, when it comes to formaldehyde, without the steric hindrance of a furan ring, the excess aldehyde will react with more amino groups, and thus MR and CMR are all negatively charged. In general, the ampholytic retanning agents are beneficial for the dyeing of leather.

Retanning Performances of MRf

Absorption, Thickening and Softness of Leather

In general, the filling ability of commercial melamine resin (CMR) is better than that of other retanning agents. However, as observed in Figure 6, the thickening of leather retanned with MRf is 10.33%, which is much higher than that of MR (6.16%) and CMR (5.94%). This, maybe, attributed to the additional rigid furan ring existing in MRf molecules. On the other hand, the softness of leather retanned by MRf was 6.05 mm, which is slightly less than that of MR (6.14 mm) and CMR (6.26 mm) respectively. This fact is reasonable because of the rigid furan

Table III
Chemical indexes of leather.

	CMR	MR	MRf
T_s before retan ($^{\circ}C$)	107.8	109.5	109.8
T_s after retan ($^{\circ}C$)	109.1	112.3	111.5
Cr_2O_3 (mg/L)	0.642	0.607	0.670
Formaldehyde (mg/kg)	181.52	178.42	Non-detectable

Table IV
Color measurements of control and experimental leathers.

	L	a	b	ΔL	ΔE
Reference	19.7	-0.1	-2.8		
CMR	23.2	0.2	-1.5	4.7	4.8
MR	23.7	0.3	-2.2	5.2	5.2
MRf	19.4	0.7	-0.4	0.9	2.3

ΔL : light difference from dyeing leathers without retanning

ΔE : total color difference, calculated by:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

ring introduced in MRf. Besides, the absorption extent of MRf (76.01%) and CMR (88.03%) were both higher than MR (68.01%).

Physical and Mechanical Characteristics of Leather

Physical and mechanical characteristics, including tensile and tear strength tests for retanned leathers, both along and across the backbone line were carried out (Table II). MRf provided leather with obviously higher tensile strength and tear strength, as compared with MR and CMR. It also can be seen that the elongation at break of MRf retanned leather is slightly lower than that of MR and CMR, consisting with their thickening and softness results. This may be due to the fact that MRf contains more functional groups which can crosslink with leather fibers.

Shrinkage Temperature of Leather, Chromium Concentration in Spent Liquor and Formaldehyde Content in Leather

As shown in Table III, the shrinkage temperatures of leather retanned with MRf, CMR or MR were obviously increased. This may be due to the interaction of retanning agents with collagen fibers through hydrogen and/or hydrophobic bonds, resulting in the increase of shrinkage temperature of leather.⁴¹ The content of chromium in spent liquors is very low, suggesting excellent fixing ability of MRf, CMR and MR for chromium in leather. Importantly, no free formaldehyde was detected in leather retanned with MRf, while CMR and MR-treated samples can be detected with free formaldehyde in the concentrations of 181.52 and 178.42mg/kg, respectively.

Color Measurements

As observed in Table IV, all of three leather samples showed positive " ΔL " value, indicating that the retanned leathers are lighter in shade. Leather retanned by MRf gets the minimum " ΔL " value among three samples, which means that it has more dark intensity. Meanwhile, the overall color difference (ΔE) of MRf retanned leather is 2.3, indicating that MRf brings very little influence in the color or shade. As pointed above, MRf is an ampholytic retanning agent, and it is in favor of the absorption of dyes.

Conclusions

In this study, furfural was used as an alternative aldehyde to react with melamine to preparation an amino resin (MRf). The retanning experiments indicated that the thickness and shrinkage temperature of leather retanned with MRf were increased due to the rigid furan ring. This ring structure imparts MRf with excellent thickening performance. Furthermore, physical and mechanical properties of leather retanned with

MRf are comparable or even better than that of formaldehyde-based MR and CMR controls. Color measurements showed that MRf retanned leather exhibited darker color, suggesting the ampholytic MRf is in favor of the absorption of dyes. These results revealed that furfural could be a potential alternative for the preparation of formaldehyde-free melamine resin through an effective, green and environmental friendly method.

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