Synthesis of a New Modified Furfural and its Application for Tanning

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Abstract: Furfural is one of the most important products of hydrolyzed plant fibre. During last century, Furfural has been used for leather tanning, because of its active aldehyde groups. As a tanning agent, besides used to make leather solely, furfural can be used to combine with chrome tannage. It also can enhance combination of chrome with collagen and reduce chrome content of the effluent from chrome tanning. Regrettably, the pity solubility in the water of furfural made a hardness to actualize tannage in the water system. In this paper, a new modified furfural which has good water solubility and tanning performance has been prepared. When it was used to tan solely, the shrinkage temperature of result leather may be about 78℃, and it also has a good softness and decentralization of collagen fibre in the case of free fatliquoring. Even when the result leather rewatered and redried, it became a little hardness, but resumed soft immediately after pinched.

Key words: furfural; modification; organic aldehyde; tanning

1 Introduction

Manufacture of organic products from biomaterial of agriculture is a topic of great importance, furfural (C_4H_3OCHO) is in the bound. In this direction, furfural, only made from plant fibre, is an interesting compound that be investigated for many years[1-10].

Furfural is an important compound in the fragrance industry, pharmacy, agriculture, and in leather manufacture[11,12]. There are two ways of producing furfural through biomass, that is, one-step method and two-step method, which depend on whether the reaction of furfural production is in the same container. In the one-step method, reaction of hydrolyze and dehydrate of pentose are completed in the same hydrolyze boiler. Be different from it, hydrolyze and dehydrate of pentose are separated in the two-step method at different temperature. Many researchers have investigated the technique of furfural synthesis[13-17]. Because of the conditions，operations and side reaction, the practical output of furfural is usually a little far from theoretic[18-19]. An advanced technique of furfural production from bagasse was investigated in this work. The better output of furfural was reached by 11%, which was 70% of the theoretic.

As literature [12] reported, furfural was a good organic tanning agent in some characteristics. Tanners at home and abroad have used furfural in the leather tanning, and brought in some pleasure results, elevation of shrink temperature and thickness of leather, reduction of chrome dosage, and mildew resistance of the result leather, etc.. Researchers in Huizhou tannery (Guangdong, China) have investigated furfural-chrome combine tanning process. They find that furfural used as the pre-tanning agent can improve the absorption of chromium, and the physical properties of result leather also accorded with request of shoes[20]. Yuan Ximing reported the use of furfural as the retanning and filling agent in chrome tanned leather, indicating that leather after furfural tanned have mildew resistance and good filling capability especially with flank[21]. All the furfural tanning researches were primary,

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detailed of furfural and furfural tanned leather weren't be studied further more. Regrettably, there was few reports about furfural tanning after then. There may some use localizations of furfural, such as the low solubility in water, irritative smell, restricted the development of furfural tannage. Aim at the disadvantage, herein, a novel modified furfural and its application for tanning is reported This is expected to result in good solubility and tanning effect. Furfural modification was chosen an organic aldehyde. The modified furfural tanned leather tested with SEM, Ts, sensory and mechanical properties.

2 Experimental

2.1 Materials

Bagasse was prior desugared and crushed into powder. All the chemicals used in this study were of analytical reagent grade. Sulfuric acid, phosphoric acid, sodium dihydrogen phosphate, bromine, salt, sodium hydroxide, 1,2-dichloroethane, organic aldehyde were obtained from KE LONG Co. (Chengdu, China). Calcium chloride was supplied by Fengcheng Co. (Shanghai, China). Pickled goat skin was prepared for tanning.

2.2 Furfural Preparation and Purification

Bagasse powder was filled into a three-necked flask and soaked in 6 wt % sulfuric acid solution for 12h. Salt (5 wt %), calcium chloride (3 wt %), phosphoric acid (1 wt %), sodium dihydrogen phosphate (1 wt %) were poured into the reactor. The mixtures were heated with a thermostatically controlled oil bath at 150℃~170℃, reflux-cooled for 2h, then circumfluence distilled for 4h. The distilled liquid was collected for extraction by using 1,2-dichloroethane (1:1/v:v), milled over 500 rpm for 1h. After leastways 5h deposited, the undersurface liquid was collected for rectification. The distillate between 158℃~164℃ was the product.

2.3 Furfural Purification and Characterization

Furfural purification was consulted with literature [1] reported. FTIR analysis for furfural was carried out on a Fourier Transform Infrared Spectrometer (Perkin Elmer Co., USA). Boiling point, refractive index and acidity of furfural were tested by using Technical Furfural Test Methods (GB 1926.2-1988).

2.4 Modification Experiments

In this procedure, furfural (10.0g) and bromine (0.5g) were added together, in the presence of Ni. After the reaction completed, sodium hydroxide solution was dropped in, changing the pH of reaction bath into alkaline. Afterwards, 5.0g organic aldehyde was poured into the reactor by heating at 80℃ for 100min.

2.5 Tanning

Pickled goat skin was symmetrical samplinged across backbone, weighed and introduced into drum with a 100% skin weight pickle solution. At the 30℃, the modified furfural (6.0~12.0 wt % of skin) was poured into drum. Using this system, the tannage can be completed in a cycle of approximately six to eight hours. After the process was performed for 4 hours, upon complete penetration, basification was carried on, so that the pH of the liquor should between 4.5 and 5.5. Leather after tanned was dried at 30℃. This work can be contrasted unmodified furfural tannage at the same condition.

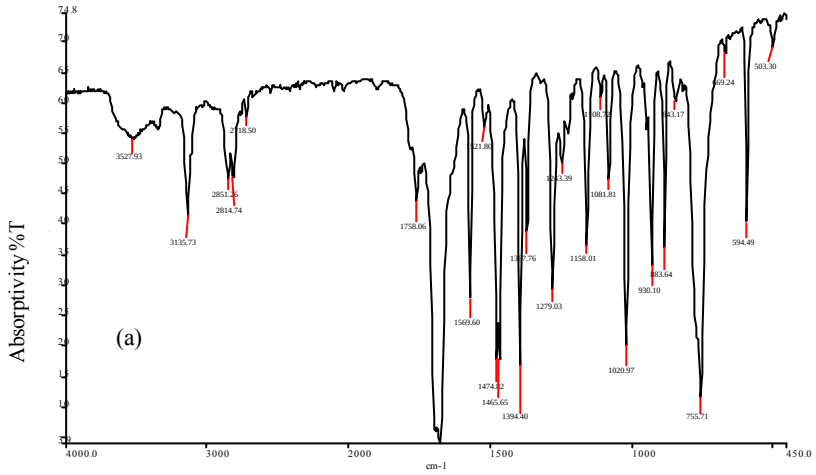
2.6 Physical Test of Tanned Leather

For physical tests, leather samples were prepared according to the standards of GB4690-84. After conditioning and measurement of thickness, the tensile strength, percentage elongation, tear load double edge tear and shrinkage temperature of the samples were tested by using Chinese Official Methods.

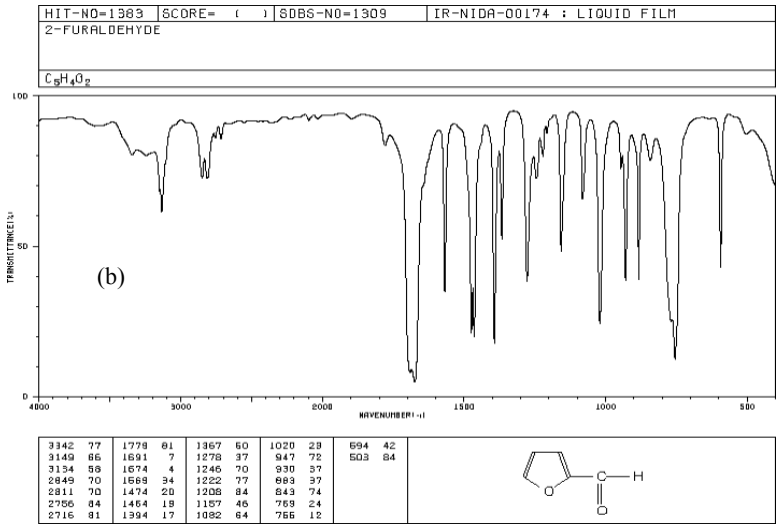
The SEM test of the cross section of end leather was test by JEOL JSM-5900LV Scanning Electron Microscope.

3 Results and discussion

Using the method of hydrolyze of bagasse into furfural we reported above, the output of furfural was reached by 11%. Some constants of furfural from this work are shown as follows: the boiling points ranged from 158.6℃ to 161.3℃, the refractive index n_D^{20} is 1.526, the acidity is 0.00755 mol·L^{-1}, and the IR spectra is quite similar to the standard (Fig. 1) .



Wavelength (cm-1)



3142	77	1779	81	1367	60	1020	28	694	42
3149	66	1691	7	1278	37	947	72	503	84
3134	58	1674	4	1246	70	930	37		
2849	70	1569	34	1222	77	883	37		
2811	70	1474	20	1208	84	843	74		
2756	84	1464	19	1157	46	769	24		
2716	81	1394	17	1082	64	766	12		

Fig. 1 IR spectra of furfural

(a) this work; (b) from Spectral Database for Organic Compounds SDBS

The water-solubility of furfural at 20℃ is 8.3%, and the modified furfural presented a better water-solubility about 20.0% and more at the same temperature. But in the analysis of the modified furfural, we find it may be a mixture; it presented tangle some peaks in the IR spectra. It is regrettable that we didn't find a good way to purify it for the time being. The later work will be carried for solve the problem.

However, the modified furfural showed some good tanning effect in the process. The contrastive tests were carried out so as to measure the tanning effect of the modified furfural. Some physical properties of

tanned leather are shown in Tab. Ⅰ. Compared with unmodified furfural, when it was used to tan solely, the modified furfural has higher shrinkage temperature (Ts/℃), better appearance and handle feel. Its elongation of 5N and 10N are even 3~4 times as unmodified furfural tanned leather's. Although the tensile strength has reduced, they are still in the range of industry standards of China (≥15 N/mm^2). Even their both tearing load are about 4 times as the standards.

Tab. 1 Sensory and mechanical properties of tanned leather

samples	Ts (℃)	Tensile strength (N/mm^2)	Elongation (%) 5N	Elongation (%) 10N	Tearing load (N/mm)	Appearance	Handle
(A)furfural	67	26.21	4.21	7.42	98.65	Filemot, glue-like	tinny,hard
(B)modified furfural 6 wt%	72	20.91	14.03	21.05	128.59	snuff color	soft, full
(C)modified furfural 12 wt%	78	22.90	18.33	25.97	103.26	snuff color, grain tightness	good feel, better fullness and flexiable

There are other prominent characteristics of the modified furfural tanned leather, which are the incrassation and softness. It can be seen in the SEM photographs of Fig. 2, the thickness of leather after tanned has increased obviously, and the collagen fibre has been better separated from. The fasciculi has been separated into piece, so as to the holes between fibre to fibre has increased evidently. In the case of free fatliquoring, the modified furfural tanned leather has good softness, even when the result leather rewatered and redried, it became a little hardness, but resumed soft immediately after pinched. This may because of the good decentralization of fibre.

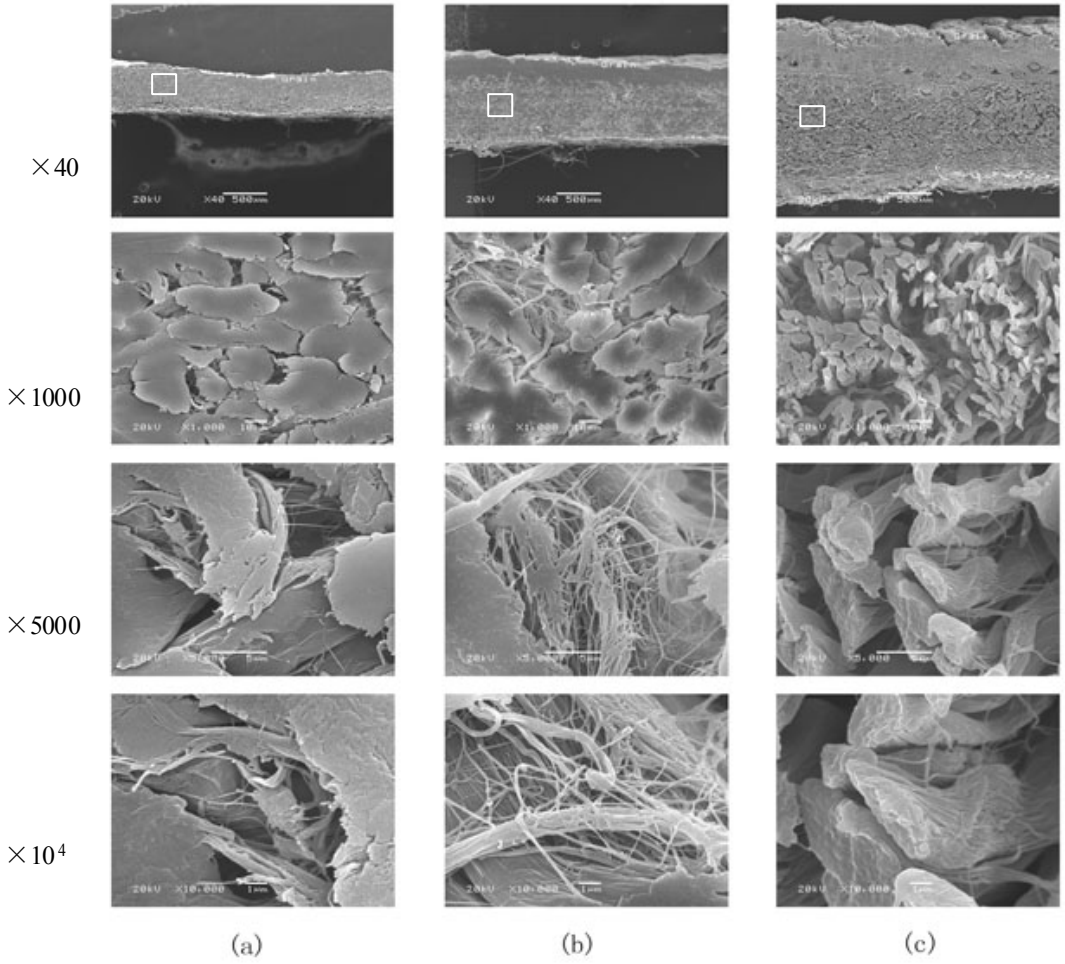


Figure 2. SEM photograph cross section of end leather
(a. furfural tanned leather; b. modified furfural tanned leather with 6 wt% of skin;
c. modified furfural tanned leather with 12 wt% of skin)

4 Conclusions

Using furfural as the tanning agent in the leather manufacture can make high value use of waste of plant fibre, and it is reproducible resource. This work synthesized a new modified furfural, which has better water-solubility and tanning effects. Modified furfural tanned leather is soft, full, flexiable, and the physical and mechanical properties are under the industry standards, except the shrinkage temperature, which may be improved on combining with other tanning agent. On all accounts, modification and tannage of furfural opened a new window to organic tanning, reference purposes only craft brother.

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