

**DEVELOPMENT OF MIMOSA TANNIN-BASED
ADHESIVE CROSS-LINKED BY FURFURYL ALCOHOL-
FORMALDEHYDE AND EPOXY RESINS**

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(RECEIVED SEPTEMBER 2018)

ABSTRACT

A furfuryl alcohol-formaldehyde resin was synthesized as a crosslinker in our laboratory to develop a mimosa tannin-based adhesive with good water resistance. ^{13}C nuclear magnetic resonance and matrix-assisted laser desorption ionization time-of-flight mass spectroscopy indicated that furfuryl alcohol reacted with formaldehyde under acidic conditions and that $-\text{CH}(-\text{OH})$ - groups to be the ones involved in the crosslinking of mimosa tannin-furfuryl alcohol-formaldehyde adhesive (TFF). The wet shear strength of TFF-bonded plywood suggested that the cured TFF adhesive was better than mimosa tannin-furfuryl alcohol (TF) adhesive. The water resistance of TFF adhesive cross-linked with 9% epoxy resin was also higher than those of TFF and TF adhesives.

KEYWORDS: Wood adhesive, tannin-based adhesive, cross-linker, water resistance, shear strength.

INTRODUCTION

Biomass materials have been widely investigated as replacements for petroleum-derived materials in related industries (Lindblad et al. 2002, Yanget al. 2017, Tondi 2017). Among these biomass materials, condensed tannin and furfuryl alcohol from forestry and agriculture have been

extracted and widely applied to tannin-based thermosetting plastic (Li et al. 2013), tannin-based rigid foam (Tondi et al. 2008a, Tondiet al. 2008b, Tondiet al. 2008c, Lacoste et al. 2013), and tannin-based grinding wheel preparation (Zhang et al. 2015, Lagel et al. 2015a, Lagel et al. 2015b).

Phenol-formaldehyde (PF) adhesive is an important synthetic resin in the wood panel industry because of its good water resistance and excellent bonding strength. However, increasing oil prices have limited the wide application of PF adhesives. As such, the substitution of tannin and furfuryl alcohol for PF adhesives (Pizzi 1980) has been explored in wood adhesive production because of their minimal toxicity; by contrast, the self-condensation of furfuryl alcohol (Pizzi et al. 2008) under acidic conditions produces tannin-furfuryl alcohol (TF) adhesives with poor water resistance. TF adhesives synthesized under alkaline conditions also exhibit a weak bonding strength (Abdullah et al. 2013). Formaldehyde can create a crosslink with furfuryl alcohol under acidic conditions to form hydroxymethyl of furfuryl alcohol, thereby decreasing the rate of self-condensation of furfuryl alcohol. In this study, tannin, furfuryl alcohol, and formaldehyde were extensively examined to synthesize a tannin-furfuryl alcohol-formaldehyde (TFF) adhesive and to prepare a bio-based wood adhesive with good water resistance for wood production. The preparation of TFF adhesives under acidic condition was also discussed. Furfuryl alcohol was co-reacted with formaldehyde to form FF resin, and TFF wood adhesive was subsequently prepared from tannins and FF resins. A commercial epoxy resin (EPR), which is presumably one of the most effective crosslinkers, was mixed with TFF adhesive and applied to plywood to develop a tannin-based adhesive with good water resistance. The feasibility of producing adhesives with enhanced water resistance was also investigated.

MATERIALS AND METHODS

Materials

Beech (*Fagus sylvatica*) veneer with a thickness of 1.5 mm and a moisture content of 9 - 10% and commercial PF adhesive with a molar ratio of F/P of 1.75 were supplied by Xinfeilin Particleboard Co., Ltd. (Yunnan, China). Mimosa (*Acacia mearnsii*, formerly *mollissima*, De Wildt) tannin extract powder was purchased from Wuning Tannin Extract Factory (Guangxi, China). Furfuryl alcohol (98% purity), formaldehyde (37% purity), and commercial EPR (E-44) were procured from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

Preparation of TF and TFF adhesives

A TF adhesive was prepared in accordance with previously described methods (Abdullah et al. 2013). The methods to achieve the following: 70 g of mimosa tannin, 35 ml of furfuryl alcohol, and 100 ml of distilled water were mixed in a beaker with stirring for 30 min at 60°C. pH was maintained at 3 by adding 30% aqueous acetic acid solution.

The TFF adhesive was prepared as follows. First, 28.9 ml of formaldehyde (37%), 35 ml of furfuryl alcohol (98%), and 100 ml of distilled water were mixed in a flat-bottomed flask with a magnetic stirrer bar at ambient temperature for 30 min to form the FF resin. pH was adjusted to 3 by adding 30% acetic acid solution. Second, 70 g of tannin was mixed with the FF resin at 60°C for 30 min to obtain the TFF adhesive.

Tab. 1: Characterization of laboratory tannin-based adhesives.

Adhesive type	Solid content (%)	Viscosity (s)	Curing time (s)
TF	37.3	52	419
TFF	48.2	73	176
PF	50.6	86	97

The weights of the solid contents of various adhesives were measured before and after they were dried in an oven at $120 \pm 1^\circ\text{C}$ for 2 h. The curing time of the TF and TFF adhesives was determined in accordance with the Chinese National Standards (GB/T14074 9-2006). The viscosities of the adhesives were tested using a TU 4 viscosity cup (Loikaw-LND-1, China). The characteristics of the different tannin-based adhesives are shown in Tab. 1.

Preparation of plywood

Beech veneers were used to prepare 300×220 mm three-layer plywood. The adhesives were brushed on both surfaces of the veneer with a glue loading of $320 \text{ g}\cdot\text{m}^{-2}$. Another test was similarly performed. Three different amounts of EPR (weight percentages of 3, 6, and 9) were added to the adhesives and stirred for 3 min and brushed on both surfaces of the veneers with a glue loading of $320 \text{ g}\cdot\text{m}^{-2}$. Subsequently, the three brushed veneers were packed together, placed in a press machine, and pressed with a press pressure of 1.5 MPa at 170°C for 5 min. Afterward, the plywood was conditioned in our laboratory at a constant temperature of $23 \pm 0.1^\circ\text{C}$ and a relative moisture content of 60% for 24 h.

Test of dry and wet shear strengths of plywood specimens

Each sample had a 25×25 mm bonded area, and the wet and dry shear strengths of the specimens were measured using an Instron 4476 universal testing machine in accordance with the Chinese National Standards (GB/T9846.7-2004). Before the wet shear strength tests were performed, the specimens were soaked in water at $63 \pm 3^\circ\text{C}$ for 1h or in boiling water for 3h. The final wet shear strength was equal to 0.82 or 0.9 of the remaining strength value. Each result was the average of eight samples.

^{13}C -NMR

A super conducting magnetic resonance imaging apparatus (Bruker-AVANCE 600, Switzerland) was used to detect the tannin-based adhesives. For the samples, $300 \mu\text{l}$ of the adhesives and $100 \mu\text{l}$ of deuterium generation solvent dimethyl sulfoxide (DMSO- d_6) were mixed. The test conditions were as follows: relaxation delay time of 6 s; accumulative number of scanning of 800 – 1200 times; and temperature of 25°C .

MALDI-TOF-MS

The different tannin-based adhesives were subjected to mass spectrometry analysis by using a KRATOS Kompact MALDI 4 instrument (AXIMA Performance, Shimadzu). Sample solutions $10 \text{ mg}\cdot\text{ml}^{-1}$ of the different adhesives in acetone were prepared. Matrix, 2,5-dihydroxybenzoic acid (C₇H₆O₄), was mixed with $10 \text{ mg}\cdot\text{ml}^{-1}$ NaCl to enhance the formation. The solutions of the adhesive and the matrix were mixed at the following proportions: 3 parts of adhesive solution, 3 parts of matrix solution, and 1 part of NaCl solution. Subsequently, $0.5 - 1 \mu\text{l}$ of the mixed solution was placed on a MALDI target. After the solvent evaporated, the MALDI target was introduced to the spectrometer. The irradiation source was a pulsed nitrogen laser with a 337 nm wavelength and the duration of a single laser pulse was 3 ns. The measurement conditions were

as follows: positive polarity, linear flight path, high mass with 20 kV acceleration voltage, and 100–150 pulses per spectrum. The delayed extraction technique was utilized by applying delay time of 200 – 800 ns.

Differential scanning calorimetry (DSC)

The curing behavior of the tannin-based adhesive was investigated using a DSC analyzer (Model DSC 204 F1, Netzsch, Germany) with a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ and a $50\text{ ml}\cdot\text{min}^{-1}$ flow of N_2 . For each test, 5 - 10 mg of a viscous prepolymer liquid was placed in an aluminum pan. The pan was then placed in the DSC machine for testing. The measuring temperature range was 30°C to 250°C .

RESULTS AND DISCUSSION

Performance of tannin-based adhesive cross-linker on the plywood

The results obtained by testing the plywood panels bonded with the tannin-based adhesives and the PF adhesive are shown in Tab. 2. The dry shear strength of the tannin-based plywood samples was according to the Chinese National Standards (GB/T9846.3-2004, $\geq 0.70\text{ MPa}$). The poor water resistance and weak shear strength of the TF adhesives were probably due to the self-condensation of furfuryl alcohol under acidic conditions, resulting in insufficient crosslinking between tannin and furfuryl alcohol. To reduce the self-condensation of furfuryl alcohol, we used formaldehyde as a coupling agent and pre-reacted it with furfuryl alcohol under acidic conditions.

In Tab. 2, the dry and wet shear strengths of the TFF adhesive were higher than those of the TF adhesive. Moreover, the water resistance of TFF remarkably improved with the addition of different EPR proportions. The water resistance of the TFF adhesive crosslinked with different proportions of EPR was better than those of the TF and TFF adhesives.

Tab. 2: Performance of tannin-based adhesives.

Adhesive Type	Dry shear strength (MPa)	Wood failure-dry condition (%)	63°C		100°C	
			Shear strength (MPa)	Wood failure (%)	Shear strength (MPa)	Wood failure (%)
TF	0.81±0.07	81	0	0	0	0
TFF	1.61±0.07	90	0.59±0.08	32	0.51±0.08	28
3%EPR+TF	0.79±0.07	81	0	0	0	0
6%EPR+TF	0.88±0.05	83	0	0	0	0
9%EPR+TF	1.23±0.08	85	0.35±0.07	0	0.33±0.05	0
3%EPR+TFF	1.64±0.07	91	0.62±0.08	37	0.60±0.07	35
6%EPR+TFF	1.72±0.08	93	0.69±0.07	75	0.63±0.09	72
9%EPR+TFF	1.83±0.08	95	0.72±0.09	88	0.73±0.06	87
PF	1.47±0.07	93	1.50±0.08	92	1.53±0.07	93

However, the plywood applied with the TF adhesive showed poor water resistance even when different EPR proportions were added. The sample of the TFF adhesive crosslinked with 9% EPR presented an excellent binding strength, and the wet shear strength at 100°C for 3 h was as high as 0.73 MPa. The dry shear strength of the TFF adhesive with 9% EPR adhesive applied on plywood was higher than that of the PF adhesive.

¹³C-NMR and MALDI-TOF-MS analysis

To investigate the reaction of furfuryl alcohol and formaldehyde or the self-condensation of furfuryl alcohol under acidic conditions, furfuryl alcohol, polymer of furfuryl alcohol resin prepared under acidic conditions, and furfuryl alcohol-formaldehyde (FF) resin were individually scanned by ¹³C NMR (Liang et al. 2018, Balakshin and Capanema 2015, Slonim et al. 1985). The results are illustrated in Figs. 1-3. The spectrum of furfuryl alcohol (Fig. 1) showed five peaks. The peak at 57.14 ppm is assigned to the hydroxymethyl of furfuryl alcohol, and the carbon absorption peaks at 156.06, 143.21, 111.49, and 108.43 ppm belong to the structure of furfuryl alcohol (Slonim et al. 1985). The $-\text{CH}_2-$ bridges in the self-condensation of furfuryl alcohol (FA- CH_2 -FA) correspond to the spectrum absorption peaks at 26–28 ppm in Figs. 2 and 3, but these peaks are not observed in Fig. 1. This finding confirmed the self-condensation of furfuryl alcohol under acidic conditions, and the reaction mechanisms are shown in Scheme 1-(1). In comparison with the spectrum of the polymer of furfuryl alcohol (Fig. 2), the region at 60–62 ppm in Fig. 3s assigned to methylene ether ($-\text{CH}-\text{O}-$) bridges between furfuryl alcohol and formaldehyde, and its reaction mechanisms are displayed in Schemes 1-(2) and 1-(3). These results indicated the crosslinking between formaldehyde and furfuryl alcohol under acidic conditions have been proven, and the competition between the reaction of furfuryl alcohol and formaldehyde and the self-condensation of furfuryl alcohol have been established. As a coupling reagent, formaldehyde was used to crosslink furfuryl alcohol and form hydroxymethyl of furfuryl alcohol. Formaldehyde also decreases the self-condensation of furfuryl alcohol.

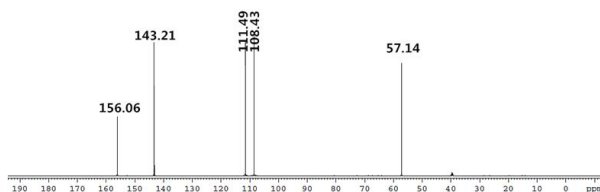


Fig. 1: ¹³C-NMR spectrum of the furfuryl alcohol.

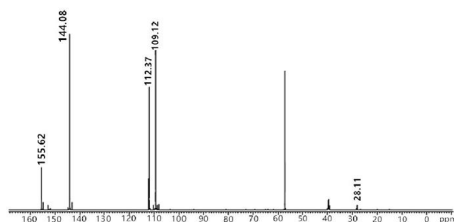


Fig. 2: ¹³C-NMR spectrum of the polymer of furfuryl alcohol resin under acid condition.

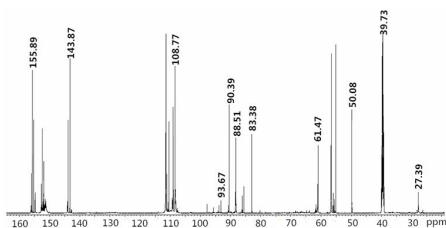
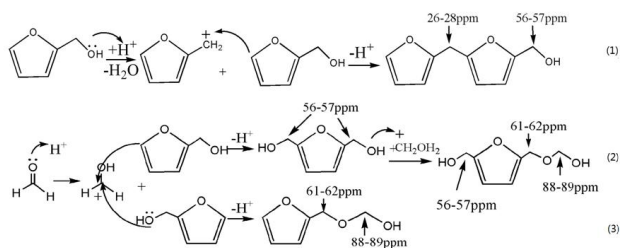


Fig. 3: ¹³C-NMR spectrum of the FF resin.



Scheme 1: The reaction mechanism of furfuryl alcohol and chemical shifts of structural groups.

The reaction the products of tannin and furfuryl alcohol have been identified (Pizzi et al. 2008). The results of the MALDI-TOF (Wei et al. 2015) analysis of the polymer of furfuryl alcohol and the different oligomers that formed the FF resin in co-polymerization between furfuryl alcohol-formaldehyde resin and mimosa tannin are shown in Figs. 4 and 5, respectively. The main chemical structures are illustrated in Tab. 3. All of the peak values are based on the relative molecular mass of the species +23 Da due to the Na^+ of the NaCl matrix enhancer used or +1 Da due to the H^+ protonation. In Figs. 4 and 5, the peaks at $m/z = 198.4$, 216.5–217.2, 397.3, 440.5, and 549.8 Da belong to the dimers, tetramers, and pentamers formed by the bridge bonding of furfuryl alcohol monomers, indicating that furfuryl alcohol indeed under went self-condensation. In comparison with the results shown in Fig. 4, the findings in Fig. 5a revealed the whole series of the oligomers at $m/z = 230.5$ and 272.5 Da, indicating a co-reaction between furfuryl alcohol and formaldehyde. The main flavonoid repeating units of mimosa tannin are fisetinidin, robinetinidin, catechin and delphinidin (Pizzi 1983, 1989). The peaks at $m/z = 303.6$ and 325.6 Da (Fig. 5a) correspond to a co-reaction between fisetinidin in monomer and formaldehyde. The peaks at $m/z = 352.4$ and 364.4 Da are attributed to the oligomers formed by furfuryl alcohol that reacts with a fisetinidin monomer (Li et al. 2013). The peaks at $m/z = 728.3$ Da (Fig. 5c) are assigned to the products of the co-reaction between fisetinidin dimers and furfuryl alcohol. The peaks at $m/z = 384.6$, 412.4, 759.9 Da, (Figs. 5b and 5c) suggest that the crosslinking between FF resin and tannin has been established (Kelley et al. 1982, Foo et al. 1985).

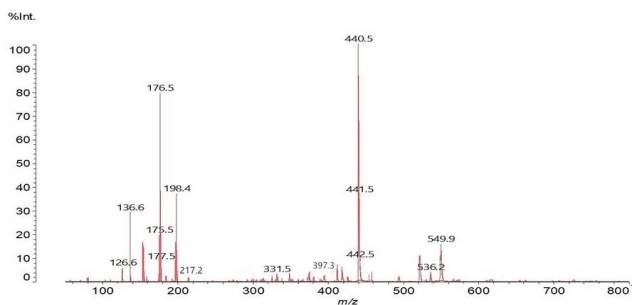


Fig. 4: MALDI-TOF peaks of the polymer of furfuryl alcohol resin under acid condition.

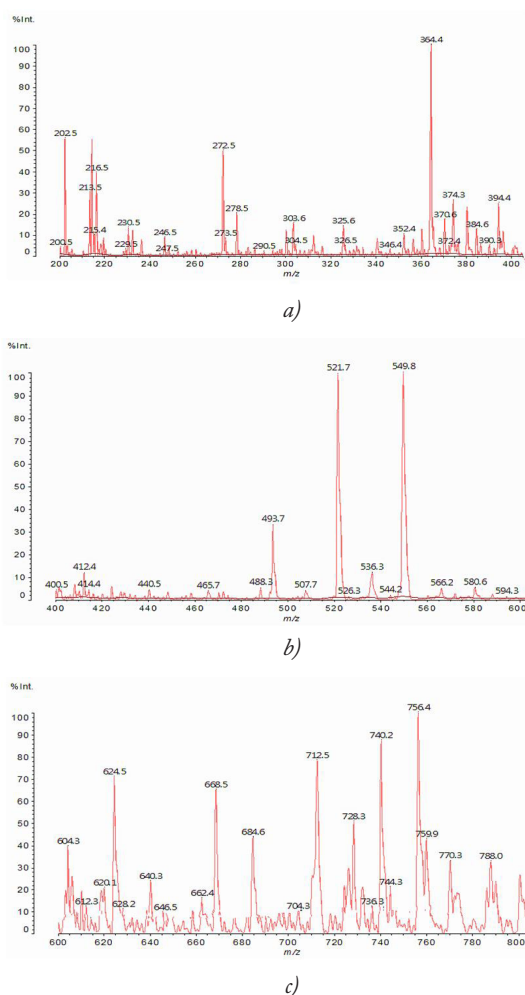
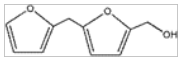
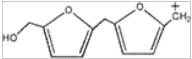
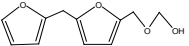
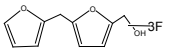
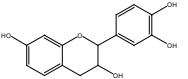
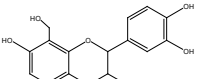
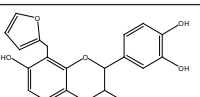
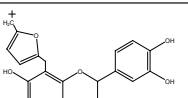
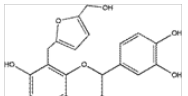
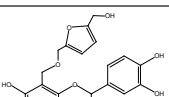
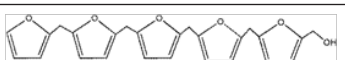

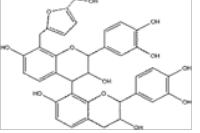
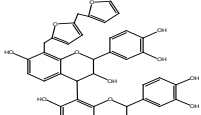
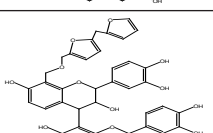


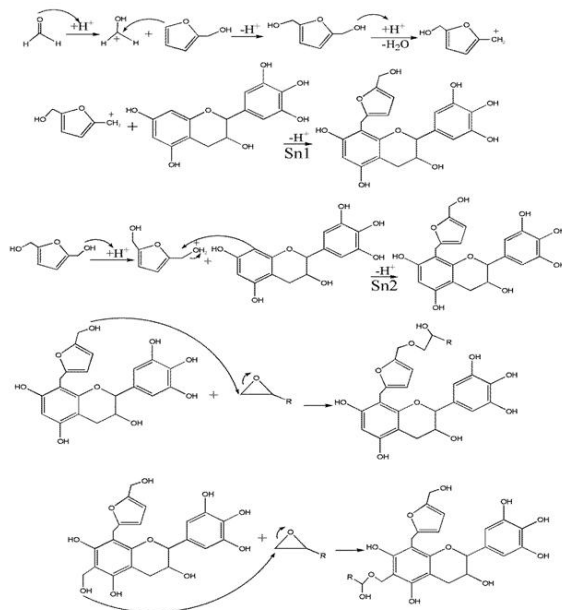
Fig. 5: MALDI-TOF peaks of the TFF resin: a) 200-400; b) 400-600; c) 600-800.

Tab. 3: Oligomers identified by MALDI-TOF mass spectrometry in the reaction of furfuryl alcohol-formaldehyde resin+mimosa tannin and self-condensation of furfuryl alcohol.

Experimental		Calculated		Chemical Species
[M+H] ⁺	[M+Na] ⁺	[M+H] ⁺	[M+Na] ⁺	
176.5/177.5	198.4	179	201	
	216.5/217.2		215	
	230.5		231	

272.5		269		
273.5		275		
303.6	325.6	305	327	
352.4		355		
364.4		367		
384.6		385		
	397.3		401	
412.4		415		
	440.5		441	
	549.8		551	
	684.6		680	
	728.3		729	
	759.9		759	

In terms of plywood performance, the water resistance of TFF with 9% EPR adhesive was better than that of the TFF adhesive. The reaction between formaldehyde and furfuryl alcohol under acidic conditions could result in the formation of hydroxymethyl in furfuryl alcohol. The formation of a crosslink between hydroxymethyl in furfuryl alcohol and tannin contributed to the formation of oligomers (Tab. 3; 384.6 and 684.6 Da). These oligomers could easily crosslink EPR under acidic conditions (Scheme 2). Meanwhile, numerous tertiary carbon hydroxylmethyls existed in TFF with 9% EPR resin could easily crosslink each other to form the three-dimensional network structure of TFG +12% EPR adhesive in the curing process. Thus, TFF with 9% EPR adhesive exhibited good water resistance.



Scheme 2: The reaction mechanism between furfuryl alcohol, tannin and formaldehyde.

DSC analysis of tannin-based adhesive cross-linked by FF resin and EPR

The typical DSC curves of EPR, TF, TFF, and TFF + 9% EPR are shown in Fig. 6.

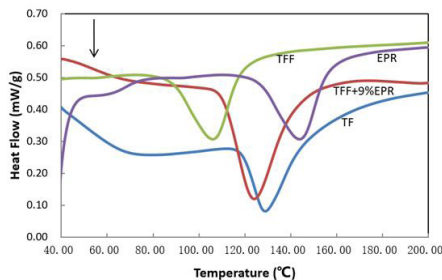


Fig. 6: DSC curves of tannin-based adhesives from 40°C to 200 °C under nitrogen adhesive, 9% EPR was mixed with TFF adhesive.

The DSC curves of EPR and TFF + 9% EPR solid resins showed broad and sharp exothermic peaks, respectively. For EPR, the first and second peaks appeared at 48°C – 76°C and 120°C - 160°C, respectively. The first peak likely occurred because of the linear self-polymerization of EPR, and the second sharp peak was probably caused by the crosslinking of the oligomers and EPR. For TFF with 9% EPR, the first peak was attributed to 48°C – 100°C as a result of the linear self-polymerization of EPR and its co-polymerization with the TFF resin. The second peak emerged at 10°C – 146°C and was generated by the oligomers that crosslinked the TFF resin with EPR.

The first peak of the TF curve at 40°C - 118°C is caused by the linear self-polymerization of furfuryl alcohol (Pizzi et al. 2008). No exothermic peaks were observed in the curves of the TFF resin and the TFF with 9% EPR resin at 4°C - 118°C. The result showed that an increase in formaldehyde in tannin and furfuryl alcohol could decrease the self-condensation of furfuryl alcohol.

CONCLUSIONS

In this study, a tannin-based wood adhesive named TFF adhesive was prepared. Definite proportions of furfuryl alcohol and formaldehyde in water were precondensed for 30 min at ambient temperature under acidic conditions. This prepolymer was then mixed with mimosa tannin at 60°C for another 30 min. ¹³C NMR and MALDI-TOF results showed that furfuryl alcohol reacted with formaldehyde and generated hydroxymethyl groups [-CH(-OH)-R-] that appeared to be the reactive groups that caused the crosslinking between tannin and FF resin. The wet shear strength of the TFF plywood was higher than that of the TF plywood. To prepare a tannin-based adhesive with an enhanced water resistance, we added 9% EPR to the TFF adhesive and found that the water resistance of the plywood with the resulting adhesive was good. The enhanced TFF adhesive could show potential for industrial wood adhesive applications.

ACKNOWLEDGMENTS

This work was supported by the Yunnan Provincial Natural Science Foundation (Grant No. 2018FG001-095), Youth Fund of the Natural Science Foundation of China (Grant No. 31800482) and Regional Fund of the Natural Science Foundation of China (Grant No. 31760187), and the Science Foundation of Southwest Forestry University (Grant No. 000033).

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