Development and Characterization of a Bayberry Tannin-based Adhesive for Particleboard

Jun Zhang,[a,b] Jiankun Liang,[a] Guanben Du,[a,b]* Xiaojian Zhou,[a] Hui Wang,[a] and Hong Lei [a]

A renewable bio-based thermosetting adhesive named tannin-furanic-formaldehyde (TFF) resin was synthesized using natural raw materials from crops and forest, such as furfuryl alcohol and bayberry tannin. The thermal properties of the adhesives were studied using differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and thermal gravimetric analysis (TGA). The structure of the TFF resin was characterized by electrospray ionization mass spectrometry (ESI-MS) and Fourier transform infrared (FTIR) spectroscopy. The results indicated that TFF resin was easily prepared. Moreover, it showed an excellent modulus of elasticity (MOE) and thermal resistance. Moreover, the cross-linking reaction of bayberry tannin, furfuryl alcohol, and formaldehyde under acid condition was established.

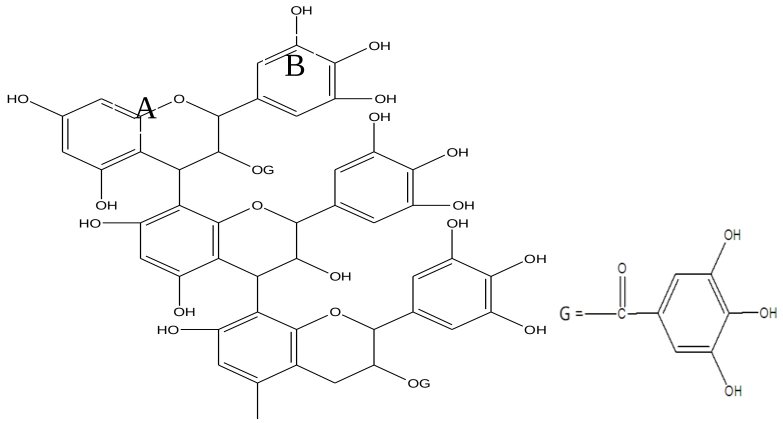
Keywords: Biosource adhesive; Tannin-based resin; Bond strength; Co-reaction

Contact information: a: Yunnan Key Laboratory of Wood Adhesives and Glue Products, Southwest Forestry University, 300 Bailong Road, Panlong District, 650224, Kunming, P.R. China; b: Key Laboratory for Forestry Resources Conservation and Utilisation in the Southwest Mountains of China, Southwest Forestry University, Ministry Education, 650224, Kunming, P.R. China;
** Corresponding author: swfudgb@163.com*

INTRODUCTION

In recent years, natural tannin and furfuryl alcohol originating from forestry and agriculture have been widely used as new bio-based materials in the polymer material industry to replace petrochemicals, such as tannin-furanic insulation foams and floral foams (Lacoste *et al.* 2013, 2014; Basso *et al.* 2014). Tannin-furanic (TF) plastics have been studied for their excellence in thermal resistance, low density, and good mechanical properties (Li *et al.* 2013). Industrial abrasive materials, such as the tannin-furanic grinding wheel (Lagel *et al.* 2015; Zhang *et al.* 2015) have been researched. Moreover, tannin-furanic wood panel adhesives have also been prepared (Abdullah and Pizzi 2013). To avoid the self-condensation of furfuryl alcohol under acid conditions, these adhesives are usually prepared under an alkaline condition to reduce the large molecules of furfuryl alcohol. In particular, the particleboards that were bonded with these adhesives prepared under alkaline conditions had a weak water resistance. Meanwhile, tannin–formaldehyde adhesives have now been developed as bio-resins for almost forty years, as it has exhibited similar performance as phenol-formaldehyde resins (Pizzi 1983). Consequently, considerable research of tannin, furfuryl alcohol, and formaldehyde have been conducted to obtain a new lower cost renewable bio-based wood adhesive with better water resistance to substitute the oil-derived wood adhesives.

Additionally, the poly-flavonoid tannin of bayberry is composed of flavonoid units, as shown in Schematic 1 (Christian *et al.* 2003; Krueger *et al.* 2003). Due to this structure, it is easy to induce cross-linking between furfuryl alcohol and formaldehyde. Hence, in this study, the possibility of preparing TFF resins based on the co-reaction of bayberry tannin, furfuryl alcohol, and formaldehyde under acid conditions was investigated. Further, the potential of the resultant adhesives to improve the water resistance property was studied and compared with a tannin-furanic adhesive.



Schematic 1. The main structure of bayberry tannin

EXPERIMENTAL

Materials

Bayberry tannin (*Myrica rubra*) in powder form was supplied by Wu Ning Tannin Extract Factory (Guanxi, China); furfuryl alcohol (with a purity of 98%), formaldehyde (with a purity of 37%), hexamethylenetetramine (with a purity of 25%), and para-toluene -4-sulphonic acid (p-TSA, 97.5%) were purchased from Acros Organics (Geel, Belgium). The particles of beech (*Fagus sylvatica*) were supplied by Xin Feiling Particleboard Company (Kunming, China).

Preparation of tannin-furanic and tannin-furanic–formaldehyde resins

Two tannin-furanic-formaldehyde resins (S1, S2) were prepared as follows: first, 70 g of tannin, 35 mL of furfuryl alcohol, and 100 mL of distilled water were mixed in a beaker and then NaOH (40%) was added under constant stirring for 2 min. The mixture was transferred into a flask and kept at 60 °C for 30 min to obtain the tannin-furanic resin (S2). Next, 28.9 mL of formaldehyde was mixed with S2 at 60 °C for 15 min to obtain the resin (S1). During the whole process, the pH was controlled at 10.

Three other tannin-furanic-formaldehyde resins (S3, S4, S5) were synthesized following this process: firstly, 70 g of tannin, 35 mL of furfuryl alcohol, and 100 mL of distilled water were mixed in a beaker and para-toluene -4-sulphonic acid was added under constant stirring for 2 min, Then, the mixture was put into a flask and kept at 60 °C for 30 min to obtain the tannin-furanic resin (S4). Next, 28.9 mL of formaldehyde were added at 60 °C and mixed with S4 for 15 min to form the resin (S3). During the process, the pH was controlled at 3. Meanwhile, the 4 mL of hexamethylenetetramine (25%) was added into the sample of S3 under stirring for 2 min to obtain the adhesive of S5.

The remaining tannin-furanic-formaldehyde resin (S6) was prepared as follows: first, 28.9 mL of formaldehyde and 35 mL of furfuryl alcohol were mixed in a beaker and para-toluene-4-sulphonic acid was added under stirring for 2 min, then the mixture was poured into a flask for reaction at 70 °C for 1 h. Next, 70 g of tannin and 100 mL of distilled water were added and the mixture was kept at 60 °C for 30 min. Then, the resin was obtained. Throughout the process, the pH was controlled at 3.

The solid content of resins was determined by measuring the weight of the resins before and after drying at a fixed oven temperature of 120 ± 1 °C for 2 h, and the viscosity of resin was measured with a tu-4 cup at 25 °C. Meanwhile, free formaldehyde content and curing time tests were implemented according to Chinese National Standard GB/T14074 (2006).

The characteristics of different resins are shown in Table 1.

Table 1. Characterization of Laboratory Tannin-based Adhesives

Adhesive Type	Solid content (%)	viscosity (s)	Curing time (s)	pH	Free formaldehyde Content (%)
S1	42	55	360	10	< 0.1
S2	37	51	480	10	0
S3	46	67	276	3	< 0.1
S4	44	58	378	3	0
S5	48	75	153	3	< 0.1
S6	35	70	225	3	< 0.15

Wood particleboards preparation

Duplicates of one layer laboratory particleboard (350 × 350 × 14 mm^3) were prepared at a temperature of 190 °C for 7.5 min using particles of beech under a maximum pressure of 28 kg/cm^2. The solid content of resin based on dry wood particles was maintained at 10%. All particleboard panels were measured for the dry internal bond (IB) strength using an Instron 4476 universal testing machine (Instron, Boston, USA) IB and thickness swelling testes were implemented according to Chinese National Standard GB/T17657 (2006). Each result was the average value of eight specimens.

Methods

Electrospray ionization mass spectrometry (ESI-MS)

A Waters Xevo Triple Quadrupole-MS (Waters, Milford, MA, USA) equipped with an electrospray ionization source (ESI) was used to perform the mass spectrometry detection. The N- (2)– L– alanyl- L- glutamine, bayberry tannin, TFF resins, and their mixture samples were dissolved in chloroform sequentially at a concentration of approximately 10 µL/mL and injected into the ESI source plus ion trap mass spectrometer (Bruker Daltonics Inc., Billerica, MA, USA) *via* a syringe at a flow rate of 5 µg/s. The spectra were recorded in a positive mode, with ion energy of 0.3 eV and scan range of 0 Da to 1000 Da.

Fourier transform infrared spectra (ftir)

A Varian1000 Infrared spectrometer (Varian, Palo Alto, CA, USA) was used to test the bayberry tannin and TFF resins. One g of KBr and 0.01 g of cured TFF adhesives were mixed to prepare the sample for testing. The test range of wave numbers was 700 cm^{-1} to 4000 cm^{-1}.

Differential scanning calorimetry (DSC)

The curing behaviors of the tannin-based adhesive on a dry basis were investigated using a DSC analyzer (Model DSC 204 F1, Netzsch, Germany) at a heating rate of 10 °C/min. The measuring temperature range was 30 °C to 250 °C with a 50 mL/min flow of N_2.

Thermomechanical analysis (TMA)

A TMA instrument (Mettler-Toledo, SDTA840, New York, USA) was used to test the TFF adhesives with The STARe software (Mettler-Toledo, Version 14.0, New York, USA) for data treatment. The temperature range was 25 °C to 250 °C. The heating rate was 20 °C/min.

Thermal gravimetric analysis (TGA)

The TGA measurement was implemented from 30 °C to 900 °C with use of a thermogravimetric analyzer (Model TG 209 F3, Netzsch, Germany). The heating rate was 20 °C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Characteristics of Laboratory Tannin-based Adhesives Bonded Particleboards

The properties of the produced particleboards from these tannin-based adhesives are gathered in Table 2. In the case of bayberry tannin-based adhesives, the dry internal bond strength (IB) was marginal according to G/BT 4897.5 (2003). Both the samples of S3 and S5 possessed high dry internal bond strength (averaged at 0.47 MPa and 0.58 MPa) and low thicknesses swelling in 2 h (averaged at 26.24% and 24.59%). The result indicated that under acid conditions, the oligomers of bayberry tannin, furfuryl alcohol, and formaldehyde easily cross-linked and caused strong bonding of S3 and S5 with TFF resins and high water resistance compared with S1 with TFF resin synthesized under alkaline condition. Meanwhile, the dry IB value of S5 was higher than that of S3, which was due to the samples modified at the end stage with 4 mL of hexamethylenetetramine. In the case of S6, because that furfuryl alcohol and formaldehyde were mixed together under a strong acid condition in the first process stage, it might involve a predominant self-polymerization of furfuryl alcohol (Tondi *et al.* 2008a, b, c) to minimize the co-condensation between tannin and furfuryl alcohol.

Table 2. Results of Laboratory Tannin-based Adhesives Bonded Particleboards

particleboard Type	IB strength, Dry (MPa)	Density (kg/m^3)	2 h Thickness Swelling (%)
S1	0.39 ± 0.05	642	34.38 ± 1.23
S2	0.34 ± 0.05	603	49.09 ± 1.39
S3	0.47 ± 0.04	623	26.24 ± 1.08
S4	0.36 ± 0.03	601	61.80 ± 2.45
S5	0.58 ± 0.05	718	24.59 ± 1.27
S6	0.34 ± 0.07	612	35.89 ± 1.58

ESI-MS Analysis

To investigate the TFF adhesive structures, the ESI-MS spectra of bayberry tannin and TFF (S3) are shown in Figs. 1 and 2. The main chemical structures are shown in Table 3. These samples contained a large number of phenolic substances, which were easily detected in the negative ion mode. The structure of polyflavonoid tannin mainly consisted of profisetinidin, procyanidins, and prodelphinidin according to the different substituent in the B-ring (Schematic 1) and also the condensation degree of the number 3 point in the C-ring with gallic acid. Figure 1 shows that the main monomer structure of bayberry tannin is prodelphinidin (456 Da), which was formed by the condensation of myricetin (305 Da) with gallic acid (169 Da). Meanwhile, 385 Da, 841 Da, 1032 Da (the difference value range was 456 Da), 689 Da, and 841 Da (the difference value range was 152 Da) corresponded to the structure of gallic acid. In Fig. 2, 169 Da, 605 Da, 881 Da, and 1032 Da were attributed to the specific structure of bayberry tannin. Moreover, 765 Da, 685 Da, and 605 Da (the difference value range was 80 Da) were attributed to the dehydration condensation product from the reaction of bayberry tannin and furfuryl alcohol. In addition, with the treatment of para-toluene -4-sulphonic acid (pTSA), some polymer structures of bayberry tannin may have been changed and were reflected by the 107 Da that corresponded to the hydroxymethyl phenol quinone, 121 Da corresponded to the hydroxymethyl quinone resorcinol, and 138 Da belonged to the hydroxymethyl benzodiazepines. The 191 Da was attributed to the condensation product of resorcinol and furfuryl alcohol, 231 Da represented the bridge bonding between the two resorcinols with methylene, which resulted in the reaction with formaldehyde. Both 213 Da and 243 Da (difference in ahydroxymethyl of formaldehyde), and 669 Da and 991 Da were attributed to the tannin-furaniccarbinol structure.

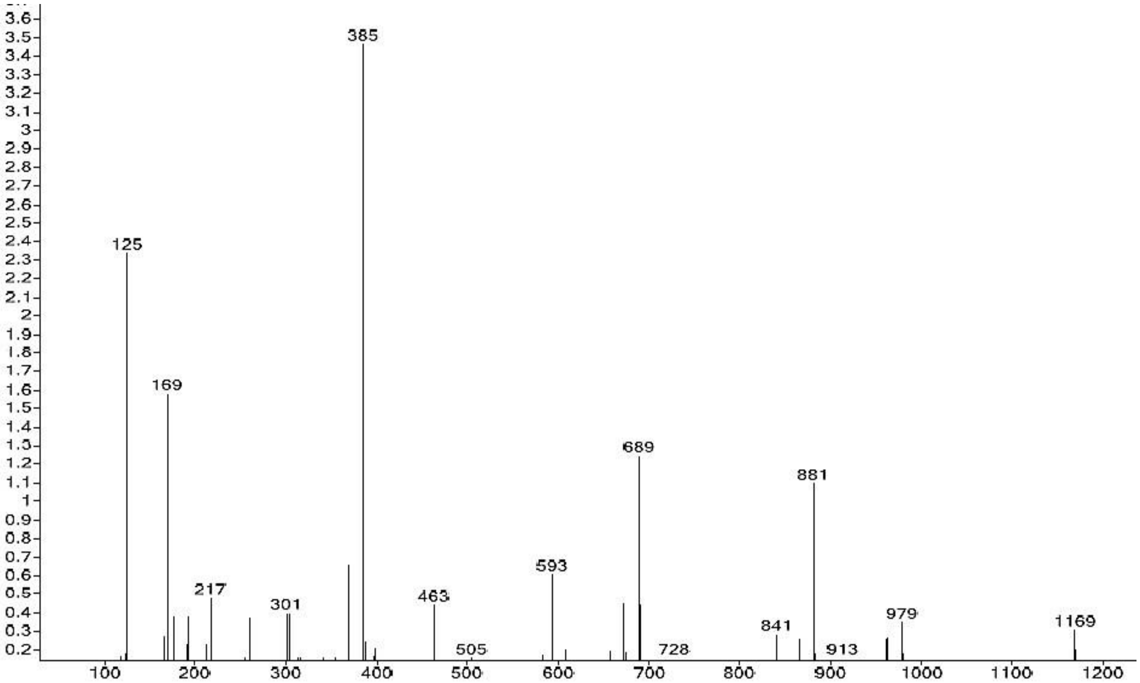


Fig. 1. ESI-MS spectra of bayberry tannin

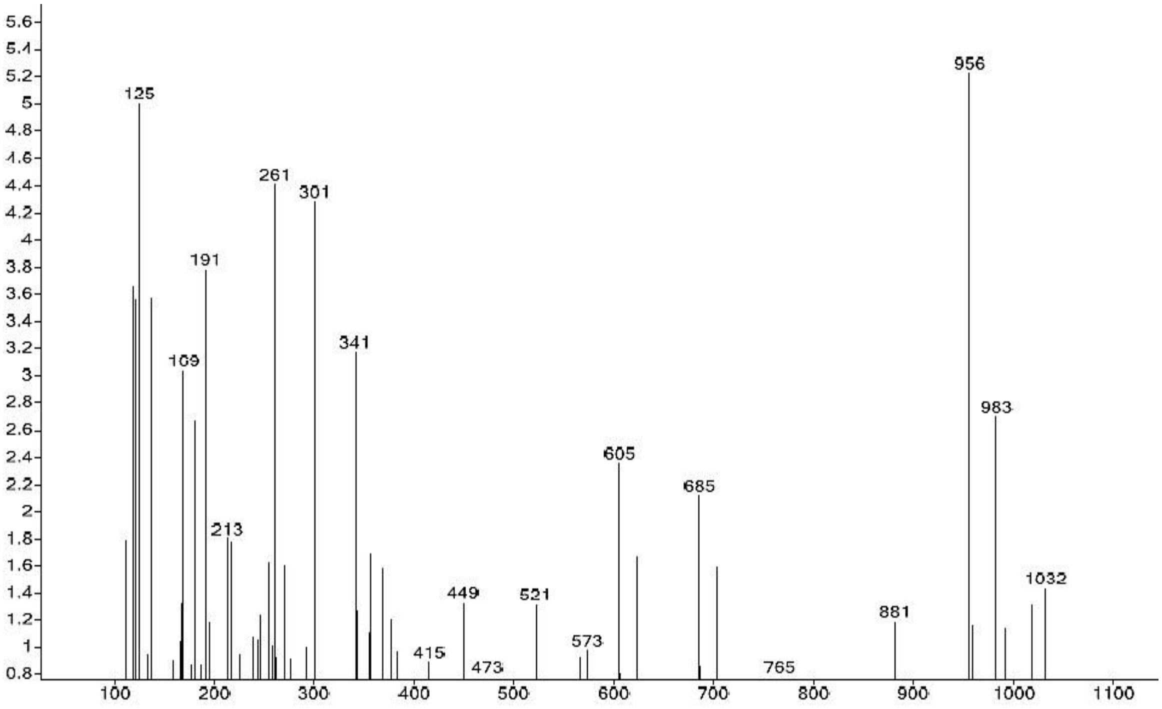
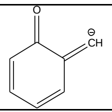
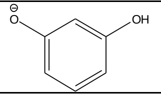
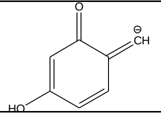
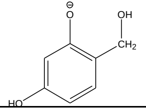
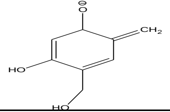
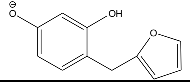
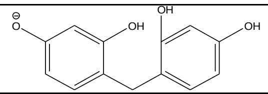
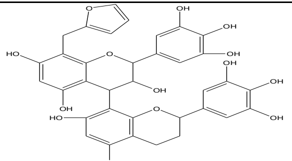
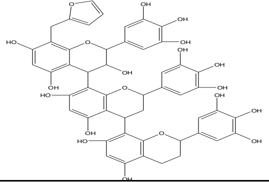
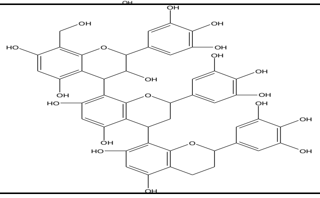


Fig. 2. ESI-MS spectra of TFF (S3) adhesive

Table 3. The Main Ion Peaks of ESI-MS and their Assignments

Experimental (Da)		Chemical Species
Sample	[M-H]-	
TFF (S3) adhesive	107	
TFF (S3) adhesive	109	
TFF (S3) adhesive	121	
TFF (S3) adhesive	138	
TFF (S3) adhesive	151	
TFF (S3) adhesive	191	

TFF (S3) adhesive	231	
TFF (S3) adhesive	669	
TFF (S3) adhesive	991	
TFF (S3) adhesive	1092	

FTIR Analysis

The infrared spectra of bayberry tannin and TFF (S3) resin are shown in Fig. 3. As shown from the bayberry tannin spectrum, the skeleton stretching vibration peak in the polyphenolic molecules of benzene ring was also found in the absorption peak points of 1672 cm^{-1} and 1450 cm^{-1}. The absorption peak of 1350 cm^{-1} and 1172 cm^{-1} corresponded to the bending vibration peak of the phenolic hydroxyl groups and the C-O stretching vibration on the benzene ring. The peaks of 1200 cm^{-1} to 1300 cm^{-1} were attributed to the ether bond (C-O-C) of the C-ring symmetry and the antisymmetric stretching vibration in tannins (Nonaka *et al.* 1981; Nasrazadani 1997).

For the TFF (S3) spectrum, the overall transmission rate was lower than that of bayberry tannin. Indeed, formaldehyde and furfuryl alcohol were added to improve the system density as well as increase the absorption of the infrared. The peaks of 1470 cm^{-1} and 1600 cm^{-1} were attributed to the benzene ring after co-reaction between the tannin, furfuryl alcohol, and formaldehyde, which indicated the stability of the benzene skeleton. Some blue and red shifts were found in the TFF spectrum compared with the spectrum of bayberry tannin, which indicated that furfuryl alcohol and formaldehyde changed the chemical environment of bayberry tannin. Moreover, it was obvious that the broad and strong peak at 1400 cm^{-1} to 1600 cm^{-1} that were attributed to the structure of prodelphinidin were seen in the bayberry tannin spectrum.

For the TFF resin spectrum, there was only one strong peak (1520 cm^{-1}), which suggested a considerable reduction in the structure of prodelphinidin. These results indicated that furfuryl alcohol and formaldehyde changed the structural characteristics of bayberry tannin.

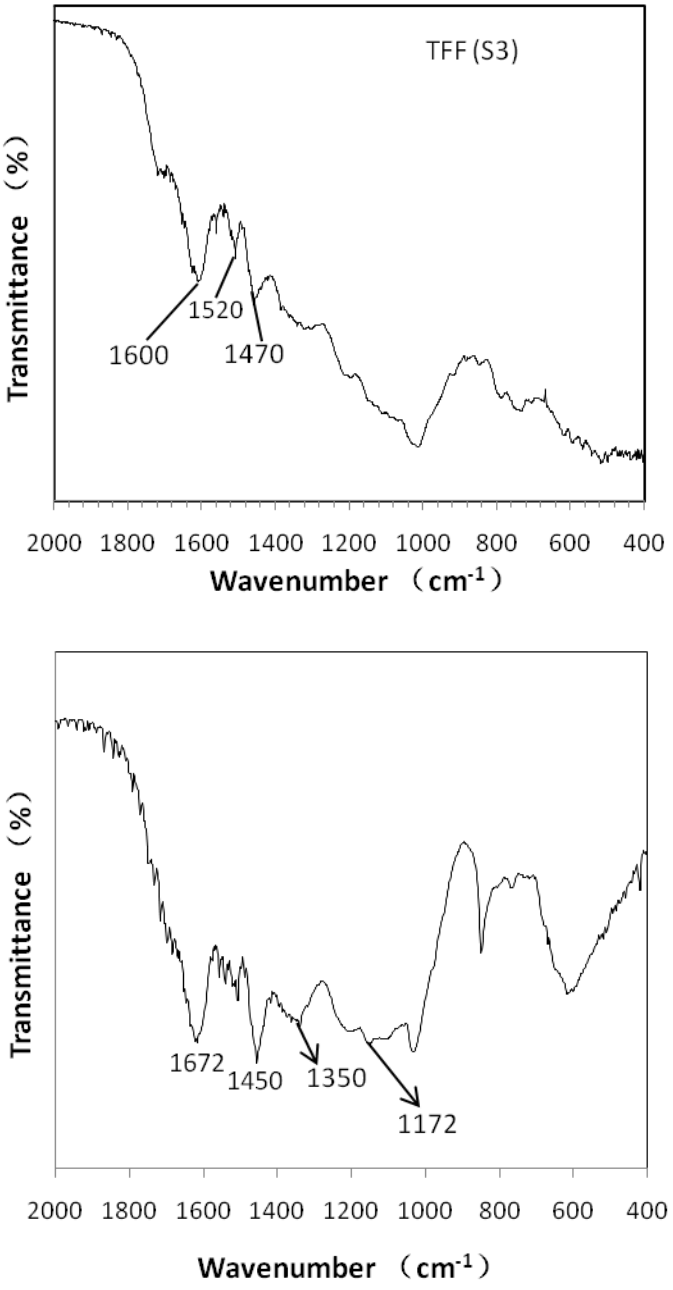


Fig. 3. The FTIR spectra of Bayberry tannin and TFF (S3) adhesive

Thermal Analysis

Typical DSC curves of TFF (S3) and TF (S4) adhesives are shown in Fig. 4. Each curve of the curing process possessed one exothermic peak, which resulted from the cross-linking reaction between the extracted tannin and furfuryl alcohol or tannin-furanic resin and formaldehyde. In addition, the values of the exothermic peaks S3 (102 °C) and S4 (106 °C) showed that the temperature when the polymerization of tannin, furfuryl alcohol, and formaldehyde reached the maximum conversion rate was lower than that of tannin and furfuryl alcohol. It was evidenced that under the treatment with formaldehyde, the bayberry tannin acquired more bonding with the furfuryl alcohol monomers.

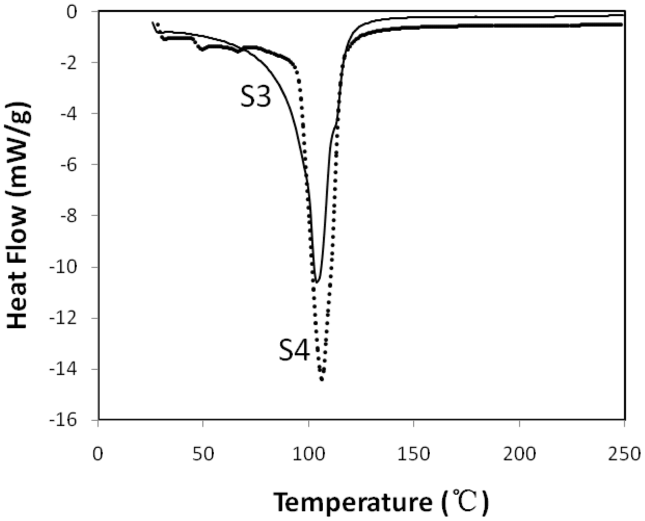


Fig. 4. DSC thermograms of the curing process of TFF (S3) and TF (S4) under nitrogen

The modulus of elasticity (MOE) results of the tannin-based adhesives with and without formaldehyde cross-linker obtained by the TMA are shown in Fig. 5. The result indicated that mixing small amounts of formaldehyde (28.9 mL) with the TF as a function of the relative proportions of TF and formaldehyde yielded a noticeable increase in MOE and achieved the maximum strength of the joints bonded with the co-reacting TFF resins. Accordingly, the IB strength of the particleboard bonded with the S3 resin was stronger than that of the particleboard bonded with S4.

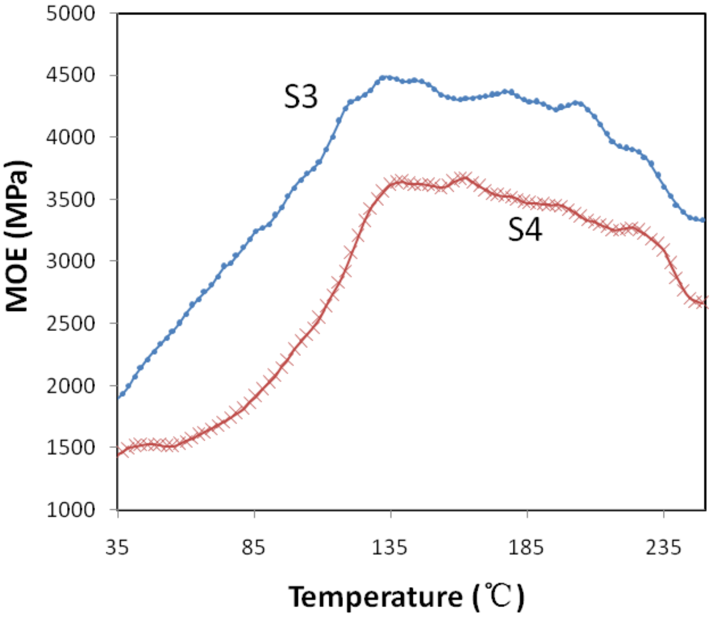


Fig. 5. Thermomechanical analysis (TMA) spectra of the TFF (S3) and TF (S4) adhesives from 35 °C to 249 °C under nitrogen

Figure 6 shows the TGA curves of the cured TFF (S3) and TF (S4) adhesives. The curves indicated that as wood adhesives, S3 and S4 had high thermal resistance. Under a nitrogen atmosphere, when the temperatures were raised to 900 °C, the weight loss of S3 and S4 were 52% and 49%, respectively. The TFF and TF resins revealed themselves as excellent carbon precursors. Especially for S3, it had 5% weight loss at 190 °C, which was higher than that of S4. Indeed, for the S3 resin, the co-reaction between tannin, furfuryl alcohol, and formaldehyde improved their thermal resistance property.

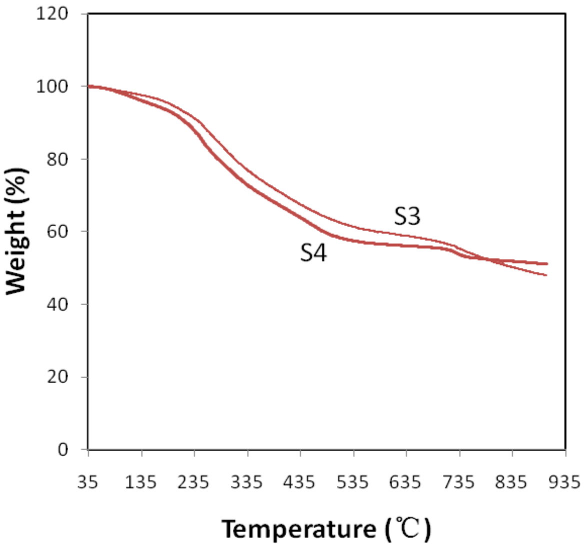


Fig. 6. TGA thermograms of the cured TFF (S3) and TF (S4) adhesives from 35 °C to 900 °C

CONCLUSIONS

1. In this paper, the performance of tannin-furanic-formaldehyde adhesive under acid condition was studied. The IB test results showed that the particleboards bonded with S3 and S5 were stronger than those bonded with other tannin-based adhesives. Moreover, the results of 2h thickness swelling declared that TFF resin synthesized under acid condition had higher water resistance than that of TFF resin prepared under alkaline condition.
2. Additionally, the ESI-MS and FTIR results indicated that the co-reaction happened between the bayberry tannin, furfuryl alcohol, and formaldehyde under acid conditions. Moreover, the DSC, TMA, and TGA results illustrated that the TFF (S3) wood adhesive had a high MOE and excellent thermal resistance. When the temperatures were raised to 900 °C, the weight residue S3 was still high at 48%.
3. The TFF adhesive (S3) was a very promising industrial natural wood adhesive and the oil-derived wood adhesive is replaceable.

ACKNOWLEDGMENTS

The authors would like to thank the Yunnan Province International Cooperation Project of China (2014IA017) and the Yunnan Province Natural Science Foundation (No. 2013Fa038) for support.

REFERENCES CITED

Abdullah, U. H., and Pizzi, A. (2013). "Tannin-furfuryl alcohol wood panel adhesives without formaldehyde," *Eur. J. Wood. Wood Prod.* 71(1), 131-132. DOI: 10.1007/s00107-012-0629-4

Basso, M. C., Giovando, S., Pizzi, A., Lagel, M. C., and Celzard, A. (2014). "Alkaline tannin rigid foams," *J. Renew. Mater.* 2, 182-185. DOI: 10.7569 / JRM. 2013. 634137

G/BT 4897.5 (2003). "Standard of particleboard using requirement in damp state," Standardization Administration of China, Beijing, China.

Krueger, C. G., Vestling, M. M., and Reed, J. D (2003). "Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry of heteropolyflavan-3-ols and glucosylated heteropolyflavans in sorghum," *J. Agric. Food Chem.* 51(3), 538-543. DOI: 10.1021/jf020746b

Lacoste, C., Basso, M. C., Pizzi, A., Laborie, M. P., Garcia, D., and Celzard, A. (2013). "Bioresourced pinetannin/furanic foams with glyoxal and glutaraldehyde," *Ind. Crop. Prod.* 45, 401-405. DOI: 10.1016/j.indcrop.2012.12.032

Lacoste, C., Pizzi, A., Laborie, M. P., and Celzard, A. (2014) "*Pinus pinaster* tannin/furanic foams: Part II. Physical properties," *Ind. Crop. Prod.* 61, 531-536. DOI: 10.1016/j.indcrop.2014.04.034

Lagel, M. C., Zhang, J., and Pizzi, A. (2015). "Cutting and grinding wheels for angle grinders with a bioresin matrix," *Ind. Crop. Prod.* 67, 264-269. DOI: 10.1016/j.indcrop.2015.01.046

Li, X. J., Nicollin, A., Pizzi, A., Zhou, X. J., and Saugeta, A. (2013). "Natural tannin–furanic thermosetting moulding plastics," *RSC Advances* 3(39), 17732-17740. DOI: 10.1039/C3RA43095B

Nasrazadani, S. (1997). "The application of infrared spectroscopy to a study of phosphoric and tannic acids interactions with magnetite (Fe304), goethite (α-FeOOH) and lepidocrocite (γ-FeOOH)," *Corrosion Science* 10-11(39), 1845-1859. DOI: 10.1016/s0010-938X (97) 00060-7

Nonaka, G. I., Nishioka, I., Nagasawa, T., and Oura, H. (1981). "Tannins and related compounds," *Chem. Pharm. Bull.* 29(10), 2862-2870. DOI: 10.1248/cpd.29.2862

Pizzi, A. (1983). "Tannin based wood adhesives," in: *Handbook of Wood Adhesive, Chemistry and Technology*, Marcel Decker Press, New York.

Tondi, G., Pizzi, A., Masson, E., and Celzard, A. (2008a). "Analysis of gases emitted during carbonization degradation of polyflavonoid tannin/furanic rigid foams," *Polymer Degradation and Stability* 93(8), 1539-1543. DOI: 10.1016/j.polymdegradstab

Tondi, G., Pizzi, A., and Olives, R. (2008b). "Natural tannin-based rigid foams as insulation for doors and wall panels," *Maderas. Ciencia y Tecnologia* 10(3), 219-227. DOI: 10.4067/S0718-221X2008000300005

Tondi, G., Pizzi, A., Pasch, H., and Celzard, A. (2008c). "Structure degradation, conservation and rearrangement in the carbonisation of polyflavonoid tannin/furanic rigid foams-A MALDI-TOF investigation," *Polymer Degradation and Stability* 93(5), 968-975. DOI: 10.1016/j.eurpolymj.2008.06.029

Zhang, J., Luo, H., Pizzi, A., Du, G. B., and Deng, S. D. (2015). "Preparation and characterization of grinding wheels based on a bioresin matrix and glass sand abrasives," *BioResources* 10(3), 5369-5380. DOI: 10.15376/biores.10.3.5369-5380

Article submitted: April 18, 2017; Peer review completed: June 24, 2017; Revised version received and accepted: June 27, 2017; Published: July 11, 2017.
DOI: 10.15376/biores.12.3.6082-6093