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# Tannin-based adhesive cross-linked by furfuryl alcohol-glyoxal and epoxy resins

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ABSTRACT

To prepare a natural tannin-based adhesive with good water resistance, an environment friendly furfuryl alcohol-glyoxal resin (FG) synthesized in the laboratory was developed as a cross-linker for tannin-based adhesives. $^{13}$C Nuclear Magnetic Resonance (NMR) and Matrix-Assisted Laser Desorption-Ionization Time-of-Flight (MALDI-TOF) mass spectroscopy results indicated that furfuryl alcohol and glyoxal reacted under acidic conditions and that the -CH-(OH)- groups could be shown to be the ones involved in the cross-linking of the tannin-furfuryl-glyoxal adhesive (TFG). The results for the wet shear strength of TFG-bonded plywood showed that the cured TFG was improved and better than that bonded with a tannin-furfuryl alcohol (TF) adhesive. Moreover, the TFG adhesive cross-linked with 12% epoxy resin (EPR) presented a good water resistance. It had a modulus of elasticity (MOE) higher than that of tannin-furfuryl alcohol-formaldehyde (TFF), TF and phenol-formaldehyde (PF) adhesives.

## 1. Introduction

During the last decades, PF wood adhesives have been widely used in the wood panel industry. However, the toxicity of free formaldehyde and phenol together with associated disposal problems have limited their further development [1,2]. Thus, with the gradually increasing needs for environment-friendly adhesives, considerable research has been conducted to develop bio-based resins coming from agricultural and forest resources such as tannin and furfuryl alcohol [3,4]. Natural condensed tannins extracted from tree bark has successfully been used to replace some petrochemical products owing to their similarity with the structure of phenol [5,6]. Furthermore, furfuryl alcohol obtained from the hydrolysis of wheat, corn and sugarcane waste has also been used to prepare polymers in industry due to the structure stability of the materials obtained and their good water resistance [7]. Nowadays biosourced materials based on tannin-furanic resins such as tannin-furanic foam [8,9], rigid plastics [10] and grinding wheels matrices [11,12] have been considerable interest to the research community. These materials present excellent mechanical properties when compared with oil-derived PF materials. However, for tannin-furanic (TF) wood panel adhesives, cross-linking is carried out under alkaline conditions to avoid wood substrate hydrolysis which would occur under acidic conditions and that the self-condensation of furfuryl alcohol predominates to such an extent to lead to little or no coreaction with tannin thus showing poor water resistance. As hydroxymethyl groups (-$CH_2$OH) are present in furfuryl alcohol, formaldehyde has been used as a cross-linker between furfuryl alcohol and tannin for tannin-furanic-formaldehyde (TFF) adhesives [4]. However, TFF adhesives are not a desirable solution as an environment-friendly adhesive because of the potential toxicity of formaldehyde. Glyoxal is a non-toxic aldehyde although less reactive than formaldehyde [13]. Consequently, research on glyoxal, furfuryl alcohol and tannin has been conducted to ascertain the feasibility of tannin-furanic-glyoxal (TFG) adhesives presenting a good bonding strength and a better water resistance. In this paper, firstly tannin, furfuryl alcohol and glyoxal were used to cross-link bio-based TFG adhesives under acid conditions. Secondly, in order to improve the water resistance of TFG, hybrid cross-linkers were established between TFG resin and a commercial epoxy resin (EPR). This study is important for the development of environment-friendly wood adhesives to replace industrial PF wood adhesives.

## 2. Experimental

### 2.1. Materials

Mimosa(*Acacia mearnsii*, formerly mollissima, De Wildt) wood tannin extract powder was purchased from Wu Ning Tannin Extract Factory (Guanxi, China). Following water extraction from the bark, the

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tannin was extracted by ethanol to eliminate the majority of carbohydrates present.

Glyoxal (with a purity of 40%), furfuryl alcohol (with a purity of 98%) and formaldehyde (with a purity of 37%) were purchased from Acros Organics(Geel, Belgium).

Beech veneer (*Fagus sylvatica*) with a 1.5 mm thickness and 9-10% moisture content was supplied by Xin Fei Lin panel Company (Kunming, China).

Commercial EPR (E-44) was purchased from Sinopharm Chemical Reagent Company (Beijing, China).

PF control adhesive (molar ratio F/P = 2.2) was supplied by Xin Fei Lin panel Company (Kunming, China).

### 2.2. Preparation of TF, TFF and TFG adhesives

The TF adhesive was synthesized according to the method of Abdullah and Pizzi [3]: 70 g of tannin, 35 mL of furfuryl alcohol and 100 of mL distilled water were mixed in a beaker under stirring for 30 min at 60 °C under alkaline conditions to form the TF adhesive. During the process, the pH was adjusted by NaOH (40%) solution to pH 10.

The TFF adhesive was prepared by the following process: 28.9 mL of formaldehyde, 35 mL of furfuryl alcohol and 100 mL of distilled water were mixed in a flat-bottom flask with a thermometer and magnetic stirrer bar at 60 °C for 30 min to obtain the furfuryl alcohol-formaldehyde (FF) resin. During this process, 30% acetic acid was used to adjust the pH to 3. After that, 70 g of tannin was added at 60 °C for 30 min to obtain the TFF adhesive.

The TFG adhesive was synthesized as follows: first, 30 mL of furfuryl alcohol, 133 mL of glyoxal and 50 mL of distilled water were mixed in a flat-bottom flask with a thermometer and stirrer at room temperature for 1 h to obtain the furfuryl alcohol-glyoxal (FG) resin. During this process, 30% acetic acid was used to adjust the pH to 4. The process is important for the decrease of furfuryl alcohol self-condensation under strong acid conditions. Second, 60 g of tannin was added into FG resin under a pH of 4 at 70 °C for 30 min to form the TFG adhesive.

The gel times and viscosities of the TF, TFF, TFG and PF adhesives were determined according to GB/T14074 9 (2006). For the gel times test, 10 g of adhesive was put into a test tube, which was then immersed in a boiling water bath (100 °C) and gently, continuously, and rapidly stirred with a muddler using an upward-downward movement until gelation occurred. The gel time was measured from the start of immersion of adhesive in boiling water. A tu-4 viscosity cup was used to test the viscosities of these adhesives. The solids content of the various adhesives were measured by determining the weight of the adhesives before and after drying at 120 ± 1 °C in an oven for 2 h. The characteristics of the different adhesives are shown in Table 1.

### 2.3. Preparation of plywood

The Beech veneers were used for the preparation of three-layer plywood of dimensions 300 mm × 220 mm × 4 mm. Firstly, adhesive was brushed onto the veneer surfaces with an adhesive loading of 320 g/m$^2$. Then three veneers were combined and put into a press and bonded under a pressure of 1.5 MPa at 170 °C for 5 min. The TFG adhesives were mixed respectively with different amounts of EPR (weight percentages of 3, 6, and 9) under stirring for 3 min before being brushed onto the surfaces of the veneers. After pressing, the plywood was conditioned in a laboratory at a constant temperature of 23 ± 0.1 °C and a relative humidity of 60% for 24 h.

**Table 1**
Characterization of laboratory tannin-based adhesives.

| Adhesive type | Solid content/% | Viscosity/(mm$^2$/s) | Gel times/s |
|---|---|---|---|
| TF | 35 | 215.25 ± 1.33 | 402 ± 3 |
| TFF | 48 | 309.41 ± 1.28 | 154 ± 4 |
| TFG | 47 | 291.48 ± 1.46 | 198 ± 4 |
| PF | 53 | 325.28 ± 1.51 | 126 ± 3 |

### 2.4. Test of dry and wet shear strengths of plywood specimens

Each plywood specimen was cut into dimensions of 100 mm × 25 mm for shear strength testing. An Instron 4476 universal testing machine was used to measure the shear strength of the specimens with each specimen having a 25 mm × 25 mm bonded area. Wet and dry shear strengths were determined respectively according to the Chinese national standards GB/T17657-1999 and CB/T9846.7-2004. Before wet shear strength testing, the specimens were immersed in water at 63 ± 3 °C for 1 h or in boiling water (100 °C) for 3 h, the final wet shear strength has to equal 0.9 of the remaining strength. Eight replicates were tested to allow calculation of mean values and standard deviations.

### 2.5. $^{13}$C-NMR

A super conducting magnetic resonance imaging apparatus (Bruker-AVANCE 600, Switzerland) was used to detect the presence of FF and FG resins. The resonance frequency employed was 150 MHz. 300 μL of samples and 100 μL dimethyl sulfoxide (DMSO - d6) solvent were mixed and assessed. Test conditions: relaxation delay time was 6 s; scanning accumulative number was 800–1200 times; and temperature of 25 °C.

### 2.6. MALDI-TOF-MS

The mass spectrometry detection of different cured tannin-based adhesives was implemented using a KRATOS Kompact MALDI 4 instrument (AXIMA Performance, Shimadzu). Firstly, different cured adhesives were dissolved in acetone (10 mg/mL). After that 2, 5-dihydroxy benzoic acid ($C_7H_6O_4$) as the matrix was mixed with NaCl (10 mg/mL) for the ion formation enhancement. The solutions of adhesive and matrix were mixed according to the proportions: 3 parts adhesive solution, 3 parts matrix solution and 1 part NaCl solution. 0.5-1 μL of the mixed solution was then placed on the MALDI target. After evaporation of the solvent, the MALDI target was introduced into 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: polarity-positive, flight path-linear, mass-high with 20 kV acceleration voltage and 100–150 pulses per spectrum. A delayed extraction technique was used by applying delay times of 200–800 ns [5].

### 2.7. Thermomechanical analysis (TMA)

The elasticity modulus (MOE) of different tannin based adhesives was obtained by a TMA instrument (Mettler-Toledo, SDTA840, New York, USA) with the STARe software (Mettler-Toledo, Version 14.0, New York, USA) for data treatment. Two beech veneers each 0.6 mm thick, bonded with each system, for a total samples dimension of 21 × 6 × 1.2 mm were tested. The heating rate was 20 °C/min and the temperature range was 25 °C–250 °C.

## 3. Results and discussion

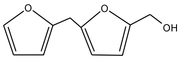
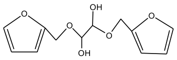
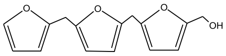
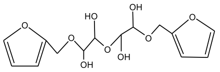
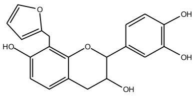
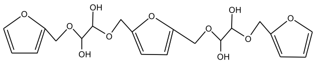
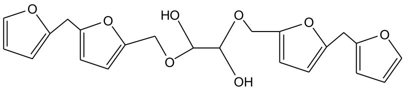
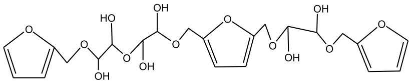
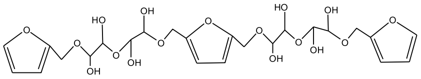
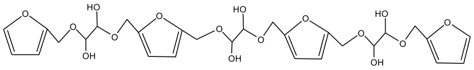
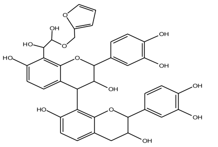
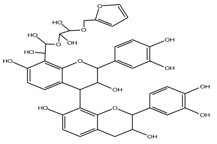
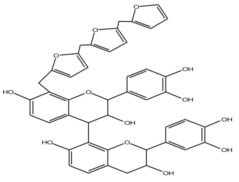
### 3.1. Characteristics of laboratory plywood bonded with tannin-based adhesives

The results obtained from testing the plywood panels bonded with these tannin-based adhesives and PF adhesive are shown in Table 2. The dry shear strength values for all of the tannin-based plywood samples were sufficient to meet the requirements of the Chinese national standard (GB/T9846.3-2004, ≥0.70 MPa). For the TF adhesive, in order to avoid the self-condensation of furfuryl alcohol [3], its synthesis was conducted under alkaline conditions. However, the panel bonded using this adhesive presented poor water resistance. To decrease the self-condensation of furfuryl alcohol and improve the water resistance of TF adhesive, glyoxal as a coupling agent was then used to react with tannin and furfuryl alcohol under acid conditions for the preparation of the TFG adhesive. Meanwhile, the TFF adhesive prepared in the laboratory was compared with the TFG adhesive. As seen from Table 3, the dry shear strength of the panel bonded with the TFF adhesive was higher than that of the panel bonded with the TFG adhesive. Furthermore, compared to the TFF adhesive-bonded panel, the TFG adhesive-bonded one showed unacceptable water resistance when placed in boiling water (100 °C) for 1 h. However, the further addition of different proportions of EPR to the TFG improved markedly its water resistance. The panel bonded with the TFG adhesive cross-

**Table 2**
Performance of tannin-based adhesives.

| Adhesive Type | Dry shear strength/MPa | 63 °C for 1 h | Boil test at 100 °C for 3 h |
|---|---|---|---|
| | | Wet shear strength/MPa | Wet shear strength/MPa |
| TF | 0.72 ± 0.09 | 0 | 0 |
| TFF | 1.65 ± 0.07 | 0.58 ± 0.09 | 0.51 ± 0.07 |
| TFG | 1.23 ± 0.08 | 0.55 ± 0.08 | 0 |
| 3%EPR + TFG | 1.56 ± 0.08 | 0.63 ± 0.08 | 0.52 ± 0.09 |
| 6%EPR + TFG | 1.61 ± 0.09 | 0.68 ± 0.09 | 0.55 ± 0.08 |
| 9%EPR + TFG | 1.69 ± 0.07 | 0.65 ± 0.07 | 0.63 ± 0.08 |
| 12%EPR + TFG | 1.82 ± 0.09 | 0.73 ± 0.07 | 0.72 ± 0.07 |
| PF | 1.67 ± 0.07 | 0.91 ± 0.08 | 0.93 ± 0.07 |

**Table 3**
Oligomers identified by MALDI-TOF mass spectrometry in the reaction of furfuryl alcohol + glyoxal + mimosa tannin.

| Experimental | | Calculated | | Chemical Species |
|---|---|---|---|---|
| $[M+H]^+$ | $[M+Na]^+$ | $[M+H]^+$ | $[M+Na]^+$ | |
| | 200 | | 201 |  |
| 254 | | 255 | |  |
| | 278 | | 281 |  |
| 312 | 334 | 313 | 335 |  |
| 356 | | 355 | |  |
| 410 | | 411 | |  |
| 414.4 | | 415 | |  |
| 468 | | 469 | |  |
| 526 | 549 | 527 | 549 |  |
| 566 | | 567 | |  |
| 704 | | 703 | |  |
| 760 | | 761 | |  |
| 788 | | 787 | |  |

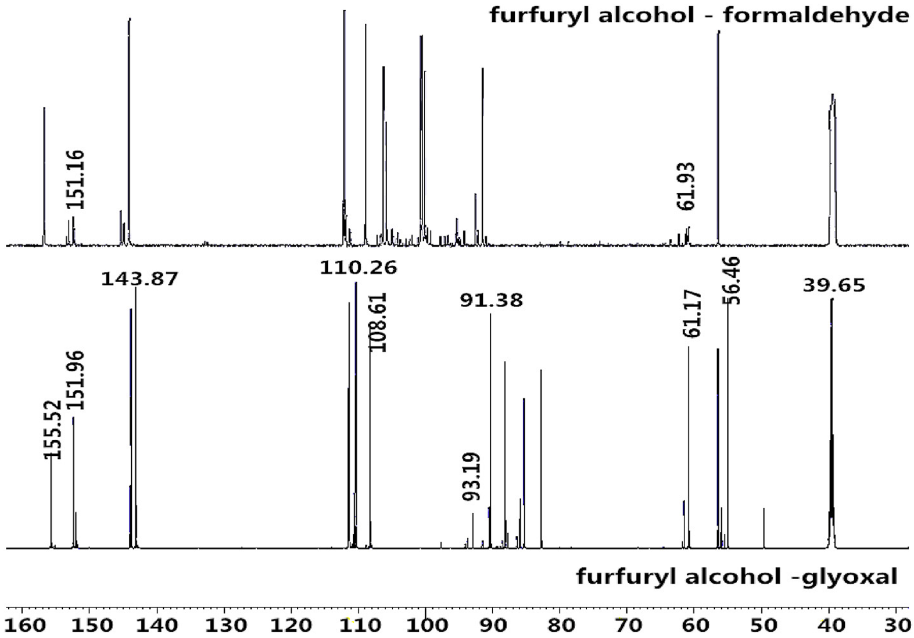


**Fig. 1.** $^{13}$C-NMR spectrum of the FF and FG resins.

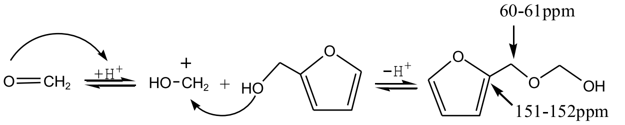
linked with 12% EPR showed good strength and its shear strength after **3** h in boiling water at 100 °C, tested wet, was as high as 0.72 MPa. In addition, the dry shear strength of the panel boned with TFG +12% adhesive was higher than that of the panel bonded with PF adhesive. On the contrary, compared with the TFG +12% adhesive, the panel bonded with PF adhesive showed a good strength after soaking in water at 63 °C or in boiling water.

Further industrial optimization for a possible future industrial production is necessary but TFG +12% EPR adhesive appears competitive with the TF and PF adhesives.

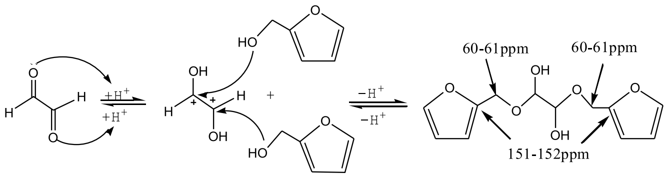
### 3.2. $^{13}$C-NMR analysis

Glyoxal was used as a coupling reagent for cross-linking with furfuryl alcohol to decrease the self-condensation of furfuryl alcohol itself. To investigate the reaction of furfuryl alcohol and glyoxal, the FG resin was scanned by $^{13}$C NMR. The FF resin was also scanned by NMR for comparison. Their NMR spectra are shown in Fig. 1. According to the literature [10,14,15], the methylene (-CH$_2$-) bridges due to furfuryl alcohol self-condensation are those corresponding to the peak region between 30 and 40 ppm. The spectrum of the FF resin, instead, does not present any peak in the 30–40 ppm region, while the self-condensation of furfuryl alcohol has appeared to have occurred by the presence of the signals at 151-152 ppm. Moreover, the 60–61 ppm shifts belong to methylene ether (-CH$_2$-O-CH$_2$-) bridges between furfuryl alcohol and formaldehyde (cf. Scheme 1).

For the spectrum of the FG resin, the peak at 56-57 ppm was attributed to the hydroxymethyl group (-CH$_2$-OH) of furfuryl alcohol, indicating that some residual resin reactivity is still present. The regions at 155–156 ppm, 142–143 ppm and 108–110 ppm belong to the structure of furfuryl alcohol. The 151–152 ppm and 60–61 ppm peaks can be attributed to the co-reaction between furfuryl alcohol and glyoxal (shown in Scheme 2), indeed similar to that of the FF resin. Conversely, no shifts between 30 and 40 ppm are observed in the spectrum of the TFG adhesive. These results indicate that cross-linking between glyoxal, or formaldehyde, and furfuryl alcohol do occur under acid conditions effectively avoiding self-condensation of furfuryl alcohol.



**Scheme 1.** The main reaction between formaldehyde and furfuryl alcohol.



**Scheme 2.** The main reaction between glyoxal and furfuryl alcohol.

In all, the -CH-(OH)-groups were established with the reaction of glyoxal with furfuryl alcohol. It could easily cross-link tannin under acid condition after curing process.

### 3.3. MALDI-ToF analysis

The results of the MALDI-TOF analysis of the different oligomers formed in the preparation of the FG and TFG resins generated by the copolymerization reaction of furfuryl alcohol, glyoxal and tannin are shown in Figs. 2 and 3. The main chemical structures of FG and TFG resins are shown in Table 3. All the peak values are based on the molecular weight (MW) of the species + 23 Da due to the Na$^+$ of the NaCl matrix enhancer used, or + 1 Da due to H$^+$ protonation [16,17]. Fig. 2 shows that the whole series of oligomers at 254 Da, 312/334 Da, 410 Da, 468 Da, 526/549 Da indicate that the co-reaction between furfuryl alcohol and glyoxal has indeed occurred. Meanwhile, the 200 Da and 278 Da peaks (shown in Fig. 3a) belong to the dimers and trimers formed by the bridge bonding of furfuryl alcohol monomers, indicating that simultaneously also the self-condensation of furfuryl alcohol has occurred. Fig. 3a and b also show some peaks at 254 Da, 312 Da, 410 Da and 526 Da, indicating that there is still some residual reactivity in the TFG resin due to the presence of still active hydroxymethyl groups (-CH$_2$-OH). The main flavonoid repeating units of mimosa tannin are fisetinidin, robinetinidin, catechin and delphinidin [18]. The 356 Da (Fig. 3a) peak belongs to oligomers formed by furfuryl alcohol reacting with a fisetinidin monomer. Moreover, the peaks at 704 Da and 760 Da (fig. 3c) can be attributed to products of the co-

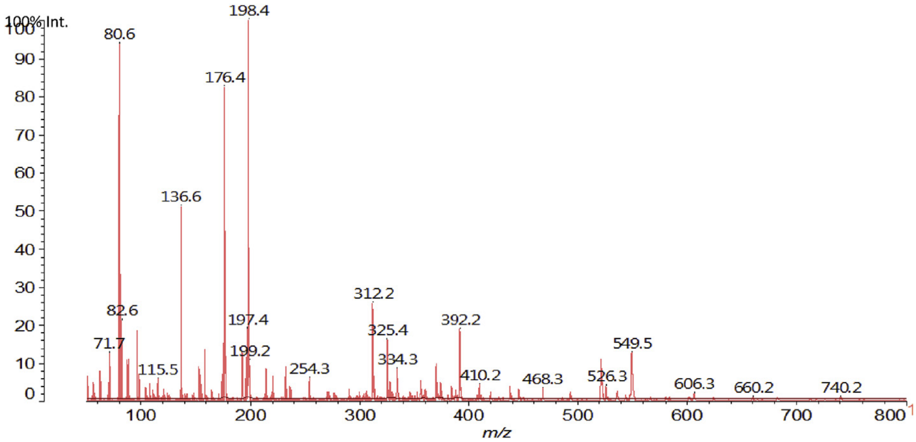


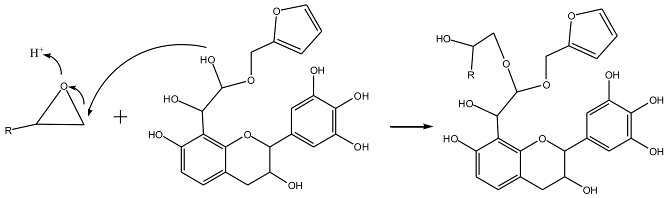
Fig. 2. MALDI-TOF peaks of the FG resin.

reaction between fisetinidin dimers, glyoxal and furfuryl alcohol monomer.

In terms of plywood performance, the water resistance of TFG +12% adhesive was better than that of the TFG adhesive, the establishment of a cross-link between FG resin and tannin contributed to the formation of oligomers (Table 3; 703 and 761 Da). These oligomers could easily cross-link EPR under acidic conditions during the curing process (Scheme 3). Numerous tertiary carbon hydroxylmethyls existed in the TFG +12% EPR adhesive. The three-dimensional network structure of TFG +12% EPR adhesive in the curing process was formed by the cross-linking of tertiary carbon hydroxylmethyls.

### 3.4. TMA analysis

The classical mechanics relation between force and deflection allowed the calculation of the Young's modulus $E$ (MOE) for each case tested [19,20].The MOE values obtained by TMA are shown in Fig. 4. The result indicates that the maximum MOE value of the TFF adhesive (1095 MPa) is higher than that of the TFG adhesive (1026 MPa). Formaldehyde added to a tannin-furfuryl alcohol system yields a higher MOE value than that of gloyxal in tannin-furfuryl alcohol. However, the addition of 12% EPR in the TFG adhesive (TFG + 12%EPR) presents a noticeable increase in MOE (1231 MPa) and achieved the maximum strength of the joints bonded with the cross-linked TFG adhesive. And it also starts to increase at a lower temperature, which means the energy of activation of hardening of the TFG + 12%EPR is apparently lower than TFF and TFG, this is confirmed by the thermomechanical analysis trace report previously [21]. Moreover, the MOE value of the TFG + 12%EPR adhesive was higher than that of the MOE value of the PF adhesive (1068 MPa).



Scheme 3. The reaction between oligomers of TFG and EPR during the curing process.

## 4. Conclusions

In this paper, a renewable tannin-furfuryl alcohol-glyoxal wood adhesive is presented. Definite proportions of furfuryl alcohol and glyoxal in water were pre-condensed for 1 h at ambient temperature under acid conditions. This pre-polymer was then mixed with mimosa

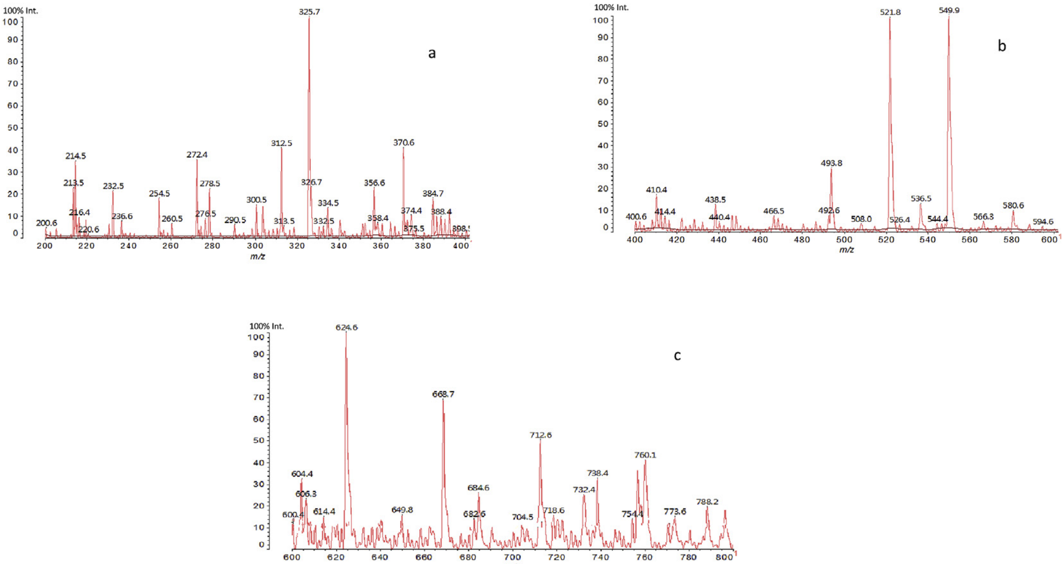


Fig. 3. MALDI-TOF peaks of the TFG resin: a) 200–400; b) 400–600; c) 600-800.

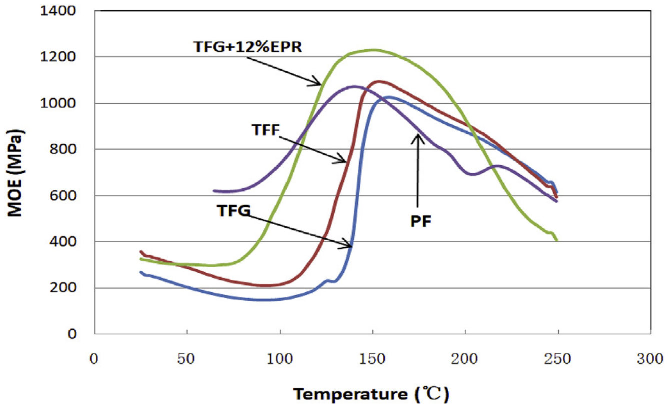


**Fig. 4.** Thermomechanical analysis (TMA) spectra of different tannin-based adhesives.

tannin at 70 °C for 30 min. The $^{13}C$ NMR and MALDI TOF results showed that there was a reaction between furfuryl alcohol and glyoxal. Moreover, the hydroxymethyl groups –CH-OH-R- generated by this reaction appeared to be the reactive groups leading to the cross-linking of TFG adhesive. The wet shear strength of TFG plywood improved compared with that of TF plywood, although the wet shear strength obtained with the TFG adhesive was lower than that with the TFF wood adhesive. In order to prepare a tannin-based adhesive with good water resistance, 12% EPR was mixed with TFG adhesive, this yielding good water resistance of the plywood. Furthermore, the MOE value of plywood prepared with 12%EPR + TFG adhesive was higher than that of plywood prepared with TF and PF adhesives.

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