Preparation and Properties of a Novel Type of Tannin-based Wood Adhesive

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Abstract:

A novel biomass-based wood adhesive was prepared with commercial Mimosa tannin extract and glycerol diglycidyl ether (GDE) by convenient mechanical mixing. GDE served as the crosslinker of the tannin without any aldehyde addition yielding hardened three-dimensional networks. Different weight ratios of tannin/GDE were investigated by a number of techniques to determine their influence on final properties. The results showed that a non-hydrolysable ester bonds can be formed between the epoxy groups of GDE and hydroxyl groups of tannin, this being the critical factor for the good water resistance obtained by the wood adhesives prepared. Moreover, the dry and wet shear strength exhibit positive correlation with the proportion of GDE added. Even at a relatively small proportion of GDE (33% of the weight of dry tannin), the dry and 24 h cold water shear strengths of the bonded plywood satisfied the requirements of relevant standard (GB/T 9846-2015, ≥ 0.7 MPa). The thermal stability of the tannin-based wood adhesive so prepared progressively improved with the increasing proportion of GDE.

Key words: Mimosa tannin, Glycerol diglycidyl ether (GDE), Biomass wood adhesive, Water resistance

1 **1 Introduction**

2 The topic of environmental and eco-friendly wood adhesive is now one of the hottest
3 subject and an unavoidable one in the wood industry^[1]. Nowadays,
4 formaldehyde-based wood adhesives are so widely applied derive from their low cost,
5 short curing time and strong adhesion^[2,3]. And the formaldehyde-based adhesives are
6 account for almost 90% of totally wood adhesives industry^[3]. Nevertheless, traditional
7 synthetic wood adhesives present two main drawbacks, these being their toxic starting
8 materials (i.e. formaldehyde and phenol) and formaldehyde-emission during their use
9 and for long time afterward. Therefore, these drawbacks have created a demand for
10 adhesives prepared from non-toxic and inexpensive materials to replace them.

11 Now, for a number of years, some biomass resources, including lignin^[4-7], tannin^[8-10],
12 protein^[11-13], non-food starch^[14,15] and agricultural or forest residues^[16-18], have
13 attracted the attention of researchers to prepare some high-performance wood
14 adhesives. Among these, condensed tannins have been considered to have some
15 interesting features to prepare wood adhesive^[19]. Initially, condensed tannins phenolic
16 nature led to their use to prepare adhesives similar to phenol-formaldehyde (PF) wood
17 adhesive^[8-10,19,20]. It is encouraging that tannin-formaldehyde wood adhesives have
18 been successful commercially for many years^[19]. However, formaldehyde, was still an
19 essential component, even though formaldehyde-emission has been improved by
20 some extent^[21]. Therefore, low or no aldehyde tannin adhesives have been developed
21 by a number of approaches. Hexamethylenetetramine (hexamine)^[22,23], glyoxal^[24],

furfuryl alcohol^[25], polymeric diphenylmethane diisocyanate (p-MDI)^[23,26], poly-ethylenimine (PEI)^[27], as well as carbohydrates-generated non-toxic and non-volatile aldehydes by specific oxidation^[28], were used to react with different condensed tannins to produce tannin-based wood adhesive without any kinds of volatile and toxic aldehydes. Certainly, some tannin wood adhesives were obtained though biomass resources (starch) mixing with condensed tannin, and alternative aldehydes acting as cross-linkers, leading to low formaldehyde emission^[13,29-31]. Apparently, these improved adhesive formulations reduced effectively the toxic raw-materials consumption and formaldehyde-emission, as well as increasing biomass content.

Herein, a novel, high-bonding performance tannin-based wood adhesive has been synthesized by manual or mechanical mixing without any pre-treatments. The cross-linker used is a commercial product, namely glycerol diglycidyl ether (GDE). Three tannin-based adhesives with different weight ratios of tannin/GDE were studied, from a high 1/1 tannin/GDE ratio to lower GDE proportions. Their properties were studied, including shear strength, hydrolysis residual rate, physico-chemical features and thermal stability. Furthermore, the reaction mechanism of tannin and GDE was confirmed by FT-IR, MALDI-TOF and solid status ¹³C NMR.

2. Materials and methods

2.1 Preparation of tannin-based wood adhesives

The series Mimosa tannin-based wood adhesives were obtained by mixing tannin and

GDE directly at room temperature without any pre-synthesis. Briefly, taking a certain amount of Mimosa tannin (*Acacia mearnsii* de Wildt) extract, supplied by Silva Chimica, St. Michele Mondovi, Italy) and then put them into a 100 mL plastic bottle. Thereafter, some amount of distilled water (Laboratory homemade) was added, stirring sufficiently by hand till a homogeneous tannin/water mixture was obtained. After that, setting a weight of glycerol diglycidyl ether (GDE, technical grade, obtained from Sigma-Aldrich) was added to the tannin/water mixture up to when a homogeneous tannin/GDE/water mixture was obtained by manual stirring. In this work, the ratio of tannin and GDE was variable, and the detailed formulations are shown in Table 1.

[Table 1 near here]

2.2 Manufacture of three-layer plywood samples and measurement of shear strength

Three-layer plywood was prepared by using tannin/GDE wood adhesives to bond poplar veneers, with single spread of 150-160 g/m², and the hot-press gluing condition are 1.25 MPa at a temperature of 160°C for 6 min. And then the dimension of fabricated plywood sample was 200 mm× 250 mm× 5 mm. All plywood samples were standby at room condition for at least 24 h before cutting. After that each sample were separated into 18 pieces of testing samples which had the dimension of 100 mm×25 mm×5 mm for measuring the dry and wet tensile force. For wet shear strength testing, the plywood samples were soaked into cold tap water for 24 h and hot water (63±3)°C

for 3 h before measuring, according to the Chinese National Standard (GB/T 17657-2013). Six repeated samples were measured for the mean values and standard deviations.

2.3 Measurement of some basic properties of tannin/GDE wood adhesives

2.3.1 pH, viscosity and solid content testing

The pH values of the series of tannin/GDE wood adhesives were measured by using PHS-3C vale meter; The viscosity of those adhesives was tested with Brookfield DV-II+ Viscometer, utilizing spindle No. 4 with 30 rpm at room condition; Taking small amount of wood adhesive samples (~3g, recorded as W_1) were putted into oven and heated them with $105\pm 2^\circ\text{C}$ till the weight difference between two adjacent times is less than 0.02 g, recorded as W_2 . The non-volatile resin solid content was calculated by the following formula:

$$\text{Solid content} = W_2 / W_1 \times 100\% \quad (1)$$

2.3.2 Hydrolysis residual rate calculating

Taking some liquid wood adhesive and put them into oven at $103\pm 2^\circ\text{C}$ till the constant weight was obtained, recorded as M_1 . And then put those dried adhesive samples into the hot water at 60°C for 6 h. After that taking the immersed samples and putting them into oven again at 105°C till the weight difference between two adjacent times is less than 0.02 g, recorded as M_2 . The residual rate was calculated by the following formula:

$$\text{Hydrolysis residual rate} = M_2 / M_1 \times 100\% \quad (2)$$

Five repeated measurement were carried out, which were calculated for the mean value and standard deviations.

2.3.3 Thermomechanical Analysis (TMA)

The relationship between modulus of elasticity (MOE) and temperature was recorded and calculated by the inner-software procedure of TMA equipment (Mettler Toledo, Zurich, Switzerland), which using three-point bending testing condition. Two pieces of beech wood, with the size of $17 \times 5 \times 1.1 \text{ mm}^3$ (Length $\times$ width $\times$ thickness), were assembled with 30 mg tannin/GDE wood adhesives to form a beech-resin-beech sandwiches structure. And then put the testing sample on the testing scaffolding. The testing was carried out between the perform temperature 30°C and 250°C with non-isothermal mode. The heating rate is $10^\circ\text{C}/\text{min}$ with a constant value. Each sample specimens were exercised a 0.1/0.5 N force cycle, which was lasted 12 seconds (6s/6s) per cycle, on an 18 mm span.

2.3.4 Thermogravimetric analysis (TGA)

The thermal stability of tannin/GDE was investigated by the TGA 5500 analysis (Mettler Toledo, Guyancourt, France). About 5-8 mg dried sample powder was putted on a platinum pan, and then heating the sample to the desire temperature at a heating rate of $10^\circ\text{C}/\text{min}$, under a nitrogen atmosphere with the flow of 50 mL/min. The testing temperature was range from 25°C to 790°C .

2.4 The reaction mechanism between tannin and GDE

2.4.1 Fourier transform infrared spectroscopy (FT-IR)

The tannin or tannin/GDE samples were cured at $120 \pm 2^\circ\text{C}$ for 2h, and then got the powder by mortar. A small amount of sample powder was placed into a diamond eye (1.8 mm) of the ATR equipment (PerkinElmer Frontier ATR-FTMIR). And then tightly screwing the clamp device, ensuring the samples were contacted with transparent glass of the bottle of diamond eye close-knit. The scan results of each sample were recorded with 32 scans between the wave range of 600 and 4000 cm^{-1} , with the scan resolution of 4 cm^{-1} .

2.4.2 Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF)

The samples for matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis were homogeneous covered on the locations dedicated analysis plaque before testing. Briefly, about 5 mg of samples were dissolved into 1 ml water/acetone mixture solution of 50:50 v/v firstly. And then, taking 10 mg of the above solution, letting them mixed with 10 μl of a 2,5-dihydroxy benzoic acid (DHB) matrix to form a homogenous mixture and standby. Before covering with samples, the corresponding of locations dedicated analysis plaque were needed to cover with 2 μl NaCl solution, which is the 0.1 M in 2:1 v/v methanol/water solution, and pre-dried. Finally, taking 1 μl sample solution and then covered on the corresponding of locations dedicated analysis plaque and dried.

Red phosphorous was act as reference sample to standardize the device before testing each time. The MALDI-TOF spectra were obtained by using the Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK). And the testing was carried out with a linear polarity-positive

tuning mode. The measurements were taken by making 1000 profiles per sample with two shots accumulated per profile. The accuracy of the spectrum is ± 1 Da.

2.4.3 Cross Polarization-Magic Angle Spinning (CP-MAS ^{13}C NMR)

To investigate the chemical structure of tannin/GDE sample, CP-MAS ^{13}C NMR equipment was utilized. The spectra result was got by the AVANCE II 400 MHz spectrometer (Brüker, Billerica, MA, USA), which using 4 mm probe at a 12-kHz sample spin. The pulse duration time was 4.1 μs at 90° , and the contact time is 2 ms with a recycling delay of 4 s. The tetramethyl silane (TMS) was served as control reference simple to determine the chemical shifts. The accuracy of the spectrum is ± 1 ppm.

3 Results and discussion

3.1 The basic characterizations of tannin/GDE wood adhesive

A novel mimosa tannin-based high-performance wood adhesive was obtained by mixing tannin with glycerol diglyceryl ether (GDE) at room temperature in distilled water. GDE was chosen as crosslinker due to its lower toxicity than other epoxies^[30-33] to provide further bond strength to the tannin. The most effective functional approach which originates from using GDE is that non-hydrolysable ether bonds can be formed with the tannin during the wood panels hot-pressing^[3]. These ethers are obtained by the reaction of the tannin -OHs with the epoxy groups of GDE by water elimination, meanwhile, they could presumably simultaneously enhance the stability of the cured resins by limiting resin degradation through hydrolytic pathways^[3]. Therefore,

tannin/GDE wood adhesives show a good bonding performance and water resistance. Table 2 shows the basic characterizations of tannin/GDE wood adhesives. The pH values are all around 5 and 5.5. There does not appear to be any major difference in solids content, all being in the 63.5% - 65.3% range. The viscosity of these adhesives, however, is significantly different, a higher viscosity being obtained for the higher proportions of tannin. The tannin: GDE weight ratios from 1:1, 2:1 and 3:1, present viscosities of 3100 ± 156 , 5600 ± 192 and 6480 ± 135 mPa·s, respectively. This indicates that GDE can effectively dilute the concentration of tannin/water solution so as to obtain a relatively lower viscosity than when the ratio of tannin/GDE is 1:1.

[Figure 1 near here]

[Table 2 near here]

3.2 Performance Analysis of tannin/GDE wood adhesive

3.2.1 Thermomechanical analysis (TMA)

The thermomechanical analysis curves have shown in Figure 2, which show the variation of Young's modulus E (MOE) as a function of curing temperature^[7,23]. A higher MOE is obtained by increasing the proportion of GDE, with the highest MOE being almost 7100 MPa when the ratio of tannin/GDE is 1:1, with the MOE becoming 5300 MPa and 4800 MPa for tannin/GDE-2/1 and tannin/GDE-3/1, respectively. This infers that tannin/GDE-1/1 gives the best bonding performance and this decreases for decreasing GDE proportions. Existing literature confirms this^[7,23,32,33]. The shear strength of bonded specimens with tannin/GDE adhesives also confirms this trend.

Even though these wood adhesives start curing at the same initial temperature, around 125°C, the highest MOE occurs at different temperatures for the different cases. Thus, for tannin/GDE-1/1, tannin/GDE-2/1 and tannin/GDE-3/1, the obtained maximum elastic modulus temperature is 170°C, 154°C and 149°C, respectively. It is most likely that more non-hydrolysable ether bonds could be formed during hot-pressing GDE increases. Therefore, more energy (a higher temperature) is needed during hot pressing to obtain a higher MOE and to form non-hydrolysable ether bonds. Figure 2 shows the MOE value sequence relationships clearly, i.e. tannin/GDE-1/1, tannin/GDE-2/1 and tannin/GDE-3/1. It can be speculated that the tannin/GDE adhesive has a higher thermal stability with higher proportion of GDE^[33]. This kind of result can be deduced from the results of the thermogravimetric analysis.

[Figure 2 near here]

3.2.2 Thermogravimetric analysis (TGA)

To investigate the thermal stability of fully cured series Tannin/GDE wood adhesives, thermogravimetric analysis (TGA) was carried out. The corresponding results curves of each samples and their first derivatives (DTG) are shown in Figure 3. There appears to be a three-stages thermal degradation process, thus, in the 50-150°C, 150-400°C and 400-600°C. DTG curves show three peaks as well, corresponding to the three thermal degradation stages. For the first one, in the low-temperature range, this weight loss was attributed to the residual water evaporation and some small molecular impurities degradation^[34,35]. The second stage occurs in the 150-400°C range, a small peak appearing in this temperature range, which corresponds to some unreacted

GDE^[3]. This is confirmed by the peak increasing at the higher proportions of GDE. Finally, the third degradation stage showing a large weight loss can occur in the 400-600°C range, is due to the degradation of the cured adhesive skeleton. Some more stable chemical bonds, such as C-C and C-O, are cleaved within this temperature range^[34-36]. Remarkably, the degradation temperature peak shifts to a higher value, while the weight loss rate shifts to smaller value with the increase in GDE. FT-IR analysis shows a new bond structure being obtained during the curing process. Thus, a new structure appears to be formed during the curing process, this contributing to improve thermal stability of the wood adhesive.

[Figure 3 near here]

3.2.3 Hydrolysis residual rate analysis

The hydrolysis residual rate is a parameter commonly used as an indicator to assess the hydrolytic stability of a cured wood adhesive^[20]. It can be calculated by using the weight difference between the original weight of an adhesive and its non-hydrolyzable portion after a specific hydrolysis treatment^[11-13]. The results for the tannin/GDE wood adhesives are shown in Table 3. As the proportion of tannin increases, the residual rate shows a decreasing trend, the lowest rate being 90.05 ± 0.037 for tannin/GDE-3/1. This indicates that the tannin/GDE-3/1 adhesive has the lowest proportion of non-hydrolysable material, thus poorer crosslinking. The residual rate increases with the decreasing amount of tannin, increased of 4% to 94.41 ± 0.031 for the tannin/GDE 2:1. This is so because of more non-hydrolysable ether bonds being formed. Same trend for the tannin/GDE-1/1 improved 6% to 96.29 ± 0.023 . These

results are consistent with other research work using epoxy resin to improve bonding performance^[37,38]. In addition, better bonding strength can be obtained by increasing GDE but unfortunately to the expense of decreasing the proportion of biomaterials.

[Table 3 near here]

3.3 The bonding performance of tannin/GDE wood adhesives

To determine the bonding performance of the tannin/GDE wood adhesive, the dry, 24 h cold water and 3 h hot water shear strengths of the plywood bonded with them were measured. The results are shown in Figure 4. It can be seen that except for the 3 h hot water treatment wet shear strength of the tannin/GDE-3/1 adhesive, all shear strength values meet the interior-use plywood requirements of China national standard (GB/T 9846-2015, ≥ 0.7 MPa). All tannin/GDE resins show an outstanding bonding performance for the dry and 24 h cold water shear strength. As expected, the shear strength of the tannin/GDE adhesives increases by increasing the amount of GDE. For the tannin/GDE-1/1 adhesive shows the highest shear strength, namely 1.61 MPa for dry strength, 1.37 MPa for 24 h cold water wet strength and 1.19 MPa for 3 h hot water shear strength, respectively. The causes of this results are more non-hydrolysable ether bonds have formed with the high amount of GDE. This conclusion is in line with the results for the residual rate. The GDE, most probably, acts in two ways: The first and most probable one is that the epoxy groups of GDE can react with -OH groups of tannin, resulting in tannin/GDE derived macromolecules forming the 3-D crosslinked network. The second one is that epoxy groups of GDE

could also react with the -OH groups of the wood panels surface, but this is the less likely possibility. Hence, the poorer trend for shear strength of tannin/GDE-2/1 and tannin/GDE-3/1 compared to the tannin/GDE-1/1 adhesive. As shown in Figure 4, the shear strength of tannin/GDE-2/1 adhesive is 1.29 MPa for dry strength, 1.07 MPa for 24 h cold water wet strength and 0.82 MPa for 3 h hot water wet strength, respectively, while the dry shear strength and 24 h cold water shear strength are 1.09 MPa and 0.83 MPa for the tannin/GDE-3/1 adhesive, these too having reached the relevant requirements. These trends are also confirmed by the results of the TMA analysis and of the residual rate. More water resistance compounds have formed during the plywood hot-pressing with high amount of GDE to yield a better wet shear strength.

[Figure 4 near here]

3.4 The reaction mechanism between tannin and GDE

3.4.1 Fourier Transform Infrared (FT-IR) spectra analysis

For investigating the functional groups changing after cured adhesives, the Fourier Transform Infrared (FT-IR) analysis was used to study the variation of functional groups after adhesives curing. The resulting spectra are shown in Figure 5. Raw tannin was used as control (black spectrum). The spectra of the tannin/GDE adhesives present a similar chemical structure than raw tannin. An intense broad absorption band (region I in Figure 5(a)) between $3200\text{--}3500\text{ cm}^{-1}$ is associated with -OH group of aromatic and aliphatic stretching vibration^[34,39,40]. Although here also have some difference between all four samples, it is still unidentifiable if some change occurs in

the number of -OH during the reaction between tannin and GDE. This is so because a new -OH group will be generated by the opening of epoxide ring when GDE reacts with the -OH group of tannin, leaving the same the apparent number of -OH groups. Some characteristic peaks can be seen in the Figure 5(b), 1607, 1508 and 1447 cm^{-1} are related to stretching vibration peaks of aromatic ring of the tannin structure^[20,41,42]. The peak at 1022 cm^{-1} represents the C-O bond stretching vibration, which probably originates from aliphatic C-OH^[20].

Some apparent changes can be noticed. In Figure 4(a), 2933 and 2860 cm^{-1} in the region II of the four samples, which are attributed to the C-H bond vibration of -CH₂- or/and -CH₃^[7,34]. Especially in the tannin/GDE wood adhesive samples, the ratio of peaks in the contoured region II are clearly greater than in the raw tannin case. These -CH₂- groups are mainly coming from the DGE and some carbohydrate impurities of the tannin extract. According to some literatures, the peak of 910 cm^{-1} should be attributed to oxirane rings if it cannot fully reaction with tannin^[43]. Nevertheless, this peak had disappeared after reaction with tannin. Therefore, one can consider that the epoxide groups of GDE have fully reacted with the tannin. Moreover, further evidence can be found in Figure 4(b) black dotted line, i.e. the peak of 1078 cm^{-1} is attributed to an ether -C-O- bond^[3], obtained by the GDE reaction with the tannin. A small peak at 1078 cm^{-1} can also be seen in the raw tannin, this being attributed to the tannin heterocycle ring. This peak has increased clearly after reaction with GDE. Therefore, these results can suggest that GDE has indeed reacted with the tannin.

[Figure 5 near here]

3.4.2 MALDI-TOF analysis

MALDI-TOF mass spectrometry is now used to determine the tannin oligomers formed and their distribution^[36,44,45]. As we all known, there are four typical oligomers, which are shown in Figure 6, i.e. Fisetinidin (272.3+2H=274.3 Da), Robinetinidin (288.3+2H=290.3 Da), Catechin (288.3+2H=290.3 Da) and Delphinidin (304.3+2H=306.3 Da), respectively, are the basic structure units of mimosa tannin-based GDE wood adhesive. Therefore, some foreseeable reaction structures can be speculated according to those monomer structural units. And the MALDI-TOF spectrum of tannin/GDE-1/1 has been done and is shown in Figure 7.

[Figure 6 near here]

From Figure 7, some regular peak-to-peak gaps can be observed, giving a sequence of peaks such as 273.9 Da, 544.4 Da and 819.4 Da; 560.5 Da and 831.0 Da; 1049.8 Da and 1320.9 Da; 1561.4 (1535.4+23) Da and 1806.8. A 272.3-274.3 Da $\pm$ 2 Da (with or without Na⁺) repeating unit is then present indicating that fisetinidin (Fi) units are present in the sample^[45,46].

Identically, a series of peaks, including 576.4 Da, 892.1 (866.7+23) Da, 1155 Da and 1443.3 Da; 784.7 Da, 1097.9 (1073+23) Da, 1631.2 Da and 1639.0 Da, were separated by a 288.3-290.3 Da $\pm$ 2 Da repeating units. Thus, robinetinidin (Ro) or catechin (Ca) repeating units, or both, are present^[10,46].

For the same reason, the presence of delphinidin (De) units at 304.3-306.3 Da $\pm$ 2 Da can be deduced from the series of peaks, such as 305.1 Da, 608.5 Da, 939.3 (914.5+23) Da and 1222.1/1220.0 Da; 803.3 Da, 1101.7 Da and 1429.6 (1409.2+23) Da^[45,46].

Moreover, because of reaction of tannin with GDE, it can more complex oligomers are also obtained. And the complex obtained-structure always derived from the tannin basic units linked by GDE. Evidence of these can be seen in Figure 7. For instance, the peak at 768.9 Da probable is that GDE act as crosslinker to linked two tannin oligomers:

Or three kinds of tannin oligomers are linked by the GDE molecules, such as the peak 1278.5 Da:

Furthermore, some large crosslinked molecules can be obtained by the present of crosslinker GDE, such as the peak at 1561 Da:

and or more complicated obtained structure, the peak at 2172.5 Da:

Hence, it can be deduced that GDE has reacted with the tannin during the curing process. The abovementioned peaks and structures are only a few representative formulas among the all peaks of MALDI-TOF spectrum, the more some foreseeable tannin or GDE derived products where been speculated and listed in Table S1.

[Figure 7 near here]

3.4.3 CP-MAS ^{13}C NMR analysis

CP-MAS ^{13}C NMR was used to investigate the tannin/GDE-1/1. The spectrum obtained is shown in Figure 8. The relatively broad and intense peak at 69.04 ppm is possibly a composite peak. It is composed of the alcohol -OHs of the carbohydrates oligomers still present in the tannin extract^[47]. This broad peak is superimposed on and composed too of the 72 ppm signal being the alcoholic -OH on the tannin heterocycle ring at C₃^[47,48]. Secondly, it is superimposed/constituted on the products from the tannin C₃-OH reacted with GDE, and possibly of the tannin extract carbohydrate residues with the GDE too, so that structures such as

-O-CH₂-CH₂OH-CH₂-R can be obtained, which should have a shift of 70.7 ppm^[44]. Therefore, the center of this composite peak at 69.04 ppm can indicate that the reaction has occurred between tannin extract components and GDE and that their reaction site is on the tannin C₃ position, but opens the possibility that the tannin extract carbohydrate residues have also reacted with GDE. In addition, the peak at 40.8 ppm is related to the -CH₂-bridges, involving the GDE or the derived products of GDE. Furthermore, a small shoulder peak at 154.45 ppm, which possible belongs to the C₅ or C₇ of A-aromatic ring^[44,47,48]. The peak at 150.14 ppm is possibly the structure obtained from the GDE reacted with tannin at the site C₅^[44], while the peak at 133.42 ppm is the C1' of flavonoid units^[47]. However, compared with the peak 69.04 ppm, it can be speculated that GDE mostly can react with tannin at its C₃ site with the clear possibility that it has reacted also with the tannin extract carbohydrates. The peak at 40.6 ppm indicates the presence of a certain extent rearrangement of the tannin to catechinic acid, an unwanted rearrangement that cannot be completely avoided^[49,50]. The peak characteristic of epoxy groups should appear at 46.4 ppm, but this kind of peak cannot be detected which indicates that the GDE has fully reacted with the tannin extract.

[Figure 8 near here]

4 Conclusions

A series of tannin-based wood adhesives were prepared via mixing commercial Mimosa tannin and GDE directly without any pre-treatment. In addition, this series of

adhesives present a good bonding performance and water resistance due to the present of non-hydrolysable ether bonds which are formed by reaction of tannin and GDE. The tannin/GDE-1/1 adhesive shows the highest shear strength, namely 1.61 MPa for dry strength, 1.37 MPa for 24 h cold water wet strength and 1.19 MPa for 3 h hot water shear strength, respectively. Moreover, the residual rate can be improved by the GDE addition and present a positive correlation trend. With the increasing of GDE addition, its residual rate passed from 90.05 for tannin/GDE-3/1 to 96.29 for tannin/GDE-1/1, hence it was improved by over 6%. Furthermore, the thermal stability has improved and exhibits the same trend as the residue rate. From the results obtained by FT-IR, MALDI-TOF and ^{13}C NMR, the typical reaction between tannin and GDE has occurred between the epoxy groups of GDE with -OH groups of the tannin extract, resulting in non-hydrolysable ether bonds. Furthermore, these ether bonds are most likely sited at the C_3 of the flavonoid units heterocyclic ring, of the carbohydrate oligomer residues in the tannin extract, and C_5 or C_7 site of A-ring, according to the ^{13}C NMR results.

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