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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],

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

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

40 **2. Materials and methods**

41 *2.1 Preparation of tannin-based wood adhesives*

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

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

53 *[Table 1 near here]*

54 ***2.2 Manufacture of three-layer plywood samples and measurement of shear***
55 ***strength***

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

64 for 3 h before measuring, according to the Chinese National Standard (GB/T
65 17657-2013). Six repeated samples were measured for the mean values and standard
66 deviations.

67 ***2.3 Measurement of some basic properties of tannin/GDE wood adhesives***

68 *2.3.1 pH, viscosity and solid content testing*

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

$$76 \text{ Solid content} = W_2 / W_1 \times 100\% \quad (1)$$

77 *2.3.2 Hydrolysis residual rate calculating*

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

$$84 \text{ Hydrolysis residual rate} = M_2 / M_1 \times 100\% \quad (2)$$

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

87 *2.3.3 Thermomechanical Analysis (TMA)*

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

98 *2.3.4 Thermogravimetric analysis (TGA)*

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

104 ***2.4 The reaction mechanism between tannin and GDE***

105 *2.4.1 Fourier transform infrared spectroscopy (FT-IR)*

106 The tannin or tannin/GDE samples were cured at $120 \pm 2^\circ\text{C}$ for 2h, and then got the
107 powder by mortar. A small amount of sample powder was placed into a diamond eye
108 (1.8 mm) of the ATR equipment (PerkinElmer Frontier ATR-FTMIR). And then
109 tightly screwing the clamp device, ensuring the samples were contacted with
110 transparent glass of the bottle of diamond eye close-knit. The scan results of each
111 sample were recorded with 32 scans between the wave range of 600 and 4000 cm^{-1} ,
112 with the scan resolution of 4 cm^{-1} .

113 *2.4.2 Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF)*

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

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

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

130 *2.4.3 Cross Polarization-Magic Angle Spinning (CP-MAS ^{13}C NMR)*

131 To investigate the chemical structure of tannin/GDE sample, CP-MAS ^{13}C NMR
132 equipment was utilized. The spectra result was got by the AVANCE II 400 MHz
133 spectrometer (Brüker, Billerica, MA, USA), which using 4 mm probe at a 12-kHz
134 sample spin. The pulse duration time was 4.1 μs at 90° , and the contact time is 2 ms
135 with a recycling delay of 4 s. The tetramethyl silane (TMS) was served as control
136 reference simple to determine the chemical shifts. The accuracy of the spectrum is \pm
137 1 ppm.

138 **3 Results and discussion**

139 *3.1 The basic characterizations of tannin/GDE wood adhesive*

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

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

158 *[Figure 1 near here]*

159 *[Table 2 near here]*

160 ***3.2 Performance Analysis of tannin/GDE wood adhesive***

161 *3.2.1 Thermomechanical analysis (TMA)*

162 The thermomechanical analysis curves have shown in Figure 2, which show the
163 variation of Young's modulus E (MOE) as a function of curing temperature^[7,23]. A
164 higher MOE is obtained by increasing the proportion of GDE, with the highest MOE
165 being almost 7100 MPa when the ratio of tannin/GDE is 1:1, with the MOE becoming
166 5300 MPa and 4800 MPa for tannin/GDE-2/1 and tannin/GDE-3/1, respectively. This
167 infers that tannin/GDE-1/1 gives the best bonding performance and this decreases for
168 decreasing GDE proportions. Existing literature confirms this^[7,23,32,33]. The shear
169 strength of bonded specimens with tannin/GDE adhesives also confirms this trend.

170 Even though these wood adhesives start curing at the same initial temperature, around
171 125°C, the highest MOE occurs at different temperatures for the different cases. Thus,
172 for tannin/GDE-1/1, tannin/GDE-2/1 and tannin/GDE-3/1, the obtained maximum
173 elastic modulus temperature is 170°C, 154°C and 149°C, respectively. It is most likely
174 that more non-hydrolysable ether bonds could be formed during hot-pressing GDE
175 increases. Therefore, more energy (a higher temperature) is needed during hot
176 pressing to obtain a higher MOE and to form non-hydrolysable ether bonds. Figure 2
177 shows the MOE value sequence relationships clearly, i.e. tannin/GDE-1/1,
178 tannin/GDE-2/1 and tannin/GDE-3/1. It can be speculated that the tannin/GDE
179 adhesive has a higher thermal stability with higher proportion of GDE^[33]. This kind of
180 result can be deduced from the results of the thermogravimetric analysis.

181 *[Figure 2 near here]*

182 3.2.2 Thermogravimetric analysis (TGA)

183 To investigate the thermal stability of fully cured series Tannin/GDE wood adhesives,
184 thermogravimetric analysis (TGA) was carried out. The corresponding results curves
185 of each samples and their first derivatives (DTG) are shown in Figure 3. There
186 appears to be a three-stages thermal degradation process, thus, in the 50-150°C,
187 150-400°C and 400-600°C. DTG curves show three peaks as well, corresponding to the
188 three thermal degradation stages. For the first one, in the low-temperature range, this
189 weight loss was attributed to the residual water evaporation and some small molecular
190 impurities degradation^[34,35]. The second stage occurs in the 150-400°C range, a small
191 peak appearing in this temperature range, which corresponds to some unreacted

192 GDE^[3]. This is confirmed by the peak increasing at the higher proportions of GDE.
193 Finally, the third degradation stage showing a large weight loss can occur in the
194 400-600°C range, is due to the degradation of the cured adhesive skeleton. Some more
195 stable chemical bonds, such as C-C and C-O, are cleaved within this temperature
196 range^[34-36]. Remarkably, the degradation temperature peak shifts to a higher value,
197 while the weight loss rate shifts to smaller value with the increase in GDE. FT-IR
198 analysis shows a new bond structure being obtained during the curing process. Thus, a
199 new structure appears to be formed during the curing process, this contributing to
200 improve thermal stability of the wood adhesive.

201 *[Figure 3 near here]*

202 *3.2.3 Hydrolysis residual rate analysis*

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

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

217 *[Table 3 near here]*

218 ***3.3 The bonding performance of tannin/GDE wood adhesives***

219 To determine the bonding performance of the tannin/GDE wood adhesive, the dry, 24
220 h cold water and 3 h hot water shear strengths of the plywood bonded with them were
221 measured. The results are shown in Figure 4. It can be seen that except for the 3 h hot
222 water treatment wet shear strength of the tannin/GDE-3/1 adhesive, all shear strength
223 values meet the interior-use plywood requirements of China national standard (GB/T
224 9846-2015, ≥ 0.7 MPa). All tannin/GDE resins show an outstanding bonding
225 performance for the dry and 24 h cold water shear strength. As expected, the shear
226 strength of the tannin/GDE adhesives increases by increasing the amount of GDE. For
227 the tannin/GDE-1/1 adhesive shows the highest shear strength, namely 1.61 MPa for
228 dry strength, 1.37 MPa for 24 h cold water wet strength and 1.19 MPa for 3 h hot
229 water shear strength, respectively. The causes of this results are more
230 non-hydrolysable ether bonds have formed with the high amount of GDE. This
231 conclusion is in line with the results for the residual rate. The GDE, most probably,
232 acts in two ways: The first and most probable one is that the epoxy groups of GDE
233 can react with -OH groups of tannin, resulting in tannin/GDE derived macromolecules
234 forming the 3-D crosslinked network. The second one is that epoxy groups of GDE

235 could also react with the -OH groups of the wood panels surface, but this is the less
236 likely possibility. Hence, the poorer trend for shear strength of tannin/GDE-2/1 and
237 tannin/GDE-3/1 compared to the tannin/GDE-1/1 adhesive. As shown in Figure 4, the
238 shear strength of tannin/GDE-2/1 adhesive is 1.29 MPa for dry strength, 1.07 MPa for
239 24 h cold water wet strength and 0.82 MPa for 3 h hot water wet strength, respectively,
240 while the dry shear strength and 24 h cold water shear strength are 1.09 MPa and 0.83
241 MPa for the tannin/GDE-3/1 adhesive, these too having reached the relevant
242 requirements. These trends are also confirmed by the results of the TMA analysis and
243 of the residual rate. More water resistance compounds have formed during the
244 plywood hot-pressing with high amount of GDE to yield a better wet shear strength.

245 *[Figure 4 near here]*

246 ***3.4 The reaction mechanism between tannin and GDE***

247 *3.4.1 Fourier Transform Infrared (FT-IR) spectra analysis*

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

256 the number of -OH during the reaction between tannin and GDE. This is so because a
257 new -OH group will be generated by the opening of epoxide ring when GDE reacts
258 with the -OH group of tannin, leaving the same the apparent number of -OH groups.
259 Some characteristic peaks can be seen in the Figure 5(b), 1607, 1508 and 1447 cm^{-1}
260 are related to stretching vibration peaks of aromatic ring of the tannin structure^[20,41,42].
261 The peak at 1022 cm^{-1} represents the C-O bond stretching vibration, which probably
262 originates from aliphatic C-OH^[20].
263 Some apparent changes can be noticed. In Figure 4(a), 2933 and 2860 cm^{-1} in the
264 region II of the four samples, which are attributed to the C-H bond vibration of -CH₂-
265 or/and -CH₃^[7,34]. Especially in the tannin/GDE wood adhesive samples, the ratio of
266 peaks in the contoured region II are clearly greater than in the raw tannin case. These
267 -CH₂- groups are mainly coming from the DGE and some carbohydrate impurities of
268 the tannin extract. According to some literatures, the peak of 910 cm^{-1} should be
269 attributed to oxirane rings if it cannot fully reaction with tannin^[43]. Nevertheless, this
270 peak had disappeared after reaction with tannin. Therefore, one can consider that the
271 epoxide groups of GDE have fully reacted with the tannin. Moreover, further evidence
272 can be found in Figure 4(b) black dotted line, i.e. the peak of 1078 cm^{-1} is attributed to
273 an ether -C-O- bond^[3], obtained by the GDE reaction with the tannin. A small peak at
274 1078 cm^{-1} can also be seen in the raw tannin, this being attributed to the tannin
275 heterocycle ring. This peak has increased clearly after reaction with GDE. Therefore,
276 these results can suggest that GDE has indeed reacted with the tannin.

277 *[Figure 5 near here]*

278 3.4.2 MALDI-TOF analysis

279 MALDI-TOF mass spectrometry is now used to determine the tannin oligomers
280 formed and their distribution^[36,44,45]. As we all known, there are four typical oligomers,
281 which are shown in Figure 6, i.e. Fisetinidin (272.3+2H=274.3 Da), Robinetinidin
282 (288.3+2H=290.3 Da), Catechin (288.3+2H=290.3 Da) and Delphinidin
283 (304.3+2H=306.3 Da), respectively, are the basic structure units of mimosa
284 tannin-based GDE wood adhesive. Therefore, some foreseeable reaction structures
285 can be speculated according to those monomer structural units. And the MALDI-TOF
286 spectrum of tannin/GDE-1/1 has been done and is shown in Figure 7.

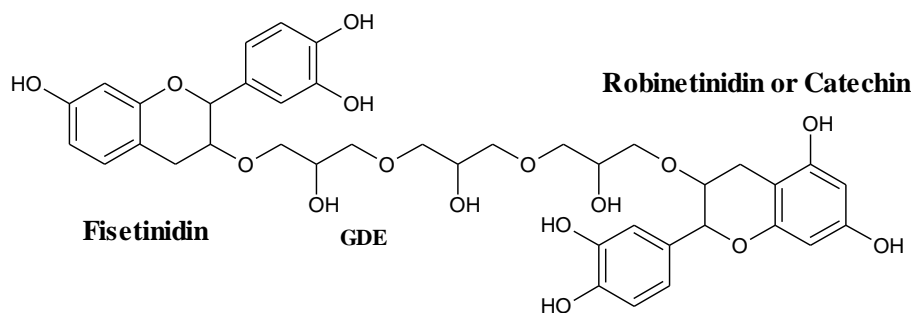
287 *[Figure 6 near here]*

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

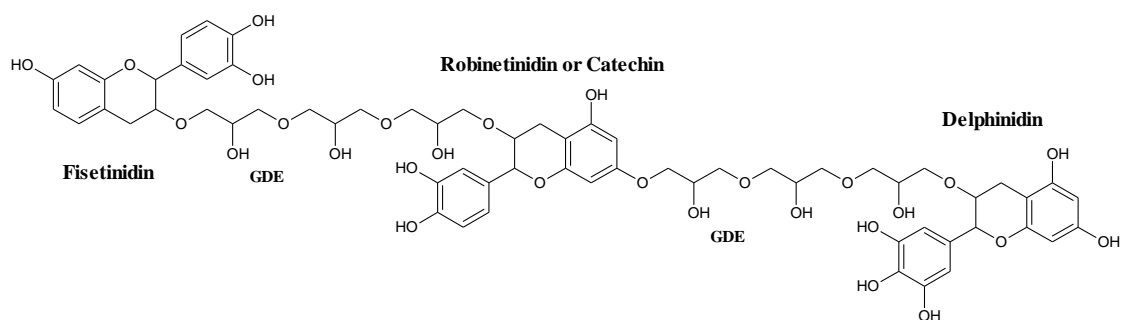
293 Identically, a series of peaks, including 576.4 Da, 892.1 (866.7+23) Da, 1155 Da and
294 1443.3 Da; 784.7 Da, 1097.9 (1073+23) Da, 1631.2 Da and 1639.0 Da, were
295 separated by a 288.3-290.3 Da \pm 2 Da repeating units. Thus, robinetinidin (Ro) or
296 catechin (Ca) repeating units, or both, are present^[10,46].

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

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

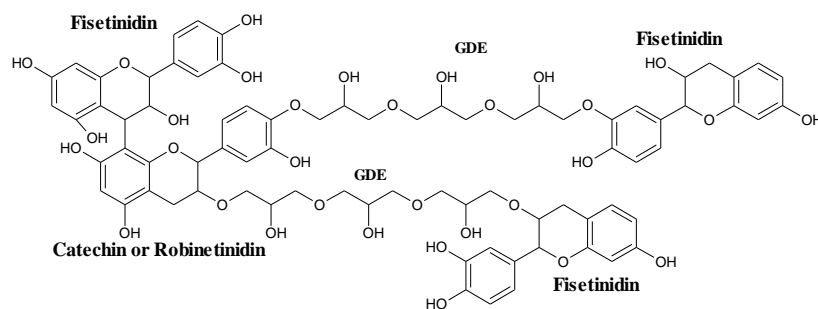


306 Or three kinds of tannin oligomers are linked by the GDE molecules, such as the peak
307 1278.5 Da:

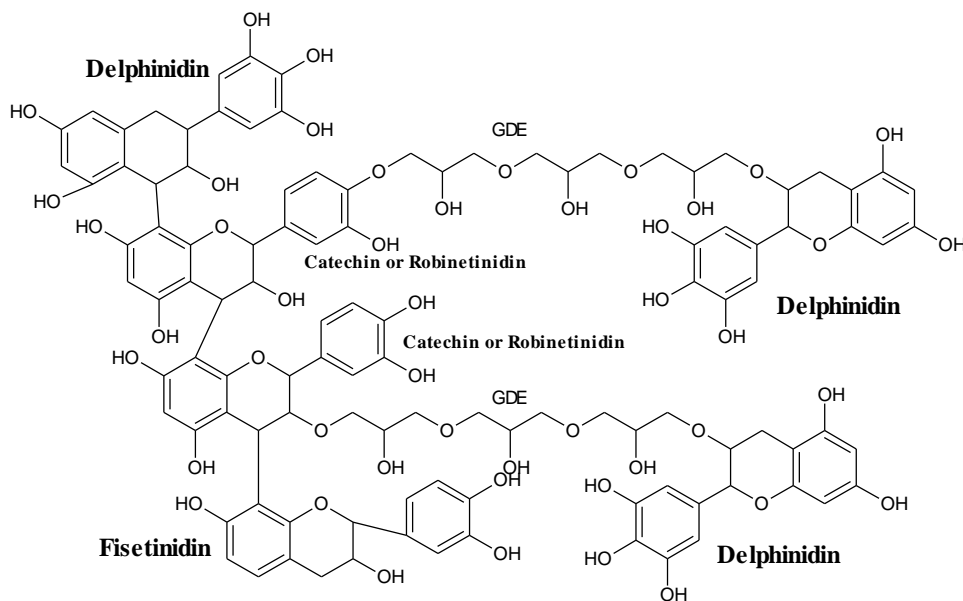


309

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



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



314

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

319 *[Figure 7 near here]*

320 3.4.3 CP-MAS ¹³C NMR analysis

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

329 -O-CH₂-CH₂OH-CH₂-R can be obtained, which should have a shift of 70.7 ppm^[44].
330 Therefore, the center of this composite peak at 69.04 ppm can indicate that the
331 reaction has occurred between tannin extract components and GDE and that their
332 reaction site is on the tannin C₃ position, but opens the possibility that the tannin
333 extract carbohydrate residues have also reacted with GDE. In addition, the peak at
334 40.8 ppm is related to the -CH₂-bridges, involving the GDE or the derived products of
335 GDE. Furthermore, a small shoulder peak at 154.45 ppm, which possible belongs to
336 the C₅ or C₇ of A-aromatic ring^[44,47,48]. The peak at 150.14 ppm is possibly the
337 structure obtained from the GDE reacted with tannin at the site C₅^[44], while the peak
338 at 133.42 ppm is the C1' of flavonoid units^[47]. However, compared with the peak
339 69.04 ppm, it can be speculated that GDE mostly can react with tannin at its C₃ site
340 with the clear possibility that it has reacted also with the tannin extract carbohydrates.
341 The peak at 40.6 ppm indicates the presence of a certain extent rearrangement of the
342 tannin to catechinic acid, an unwanted rearrangement that cannot be completely
343 avoided^[49,50]. The peak characteristic of epoxy groups should appear at 46.4 ppm, but
344 this kind of peak cannot be detected which indicates that the GDE has fully reacted
345 with the tannin extract.

346 *[Figure 8 near here]*

347 **4 Conclusions**

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

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

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372 **6 References**

373 [1] Wilson, J.B. Life-cycle inventory of medium density fiberboard in terms of
374 resources, emissions, energy and carbon. *Wood and Fiber Science*, **2010**, 42(CORRIM
375 Special Issue), 107-124.

376 [2] Salthammer, T.; Mentese, S.; Marutzky, R. Formaldehyde in the indoor
377 environment. *Chemical reviews*, **2010**, 110(4), 2536-2572. DOI: 10.1021/cr800399g.

378 [3] Li, R.J.; Gutierrez, J.; Chung, Y. L.; Frank, C. W.; Billington, S. L.; Sattely, E. S.
379 A lignin-epoxy resin derived from biomass as an alternative to formaldehyde-based
380 wood adhesives. *Green chemistry*, **2018**, 20(7), 1459-1466. DOI:10.1039/c7gc03026f
381 (2018).

382 [4] Aziz, N. A.; Latip, A. F. A.; Peng, L. C.; Abd Latif, N. H.; Brosse, N.; Hashim, R.;
383 Hussin, M. H. Reinforced lignin-phenol-glyoxal (LPG) wood adhesives from coconut
384 husk. *International journal of biological macromolecules*, **2019**, 141, 185-196. DOI:
385 10.1016/j.ijbiomac.2019.08.255.

386 [5] Chen, H.; Nair, S. S.; Chauhan, P.; Yan, N. Lignin containing cellulose nanofibril
387 application in pMDI wood adhesives for drastically improved gap-filling properties
388 with robust bondline interfaces. *Chemical Engineering Journal*, **2019**, 360, 393-401.
389 DOI: 10.1016/j.cej.2018.11.222.

390 [6] Hussin, M. H.; Aziz, A. A.; Iqbal, A.; Ibrahim, M. N. M.; Abd Latif, N. H.
391 Development and characterization novel bio-adhesive for wood using kenaf core

392 (Hibiscus cannabinus) lignin and glyoxal. *International journal of biological*
393 *macromolecules*, **2019**, 122, 713-722. DOI: 10.1016/j.ijbiomac.2018.11.009.

394 [7] Chen, X.; Xi, X.; Pizzi, A. ; Fredon, E. ; Du, G. ; Gerardin, C.; Amirou, S.
395 Oxidized demethylated lignin as a bio-based adhesive for wood bonding. *The Journal*
396 *of Adhesion*, **2020**, 1-18. DOI: 10.1080/00218464.2019.1710830.

397 [8] Hoong, Y.B.; Paridah, M.T.; Luqman, C. A.; Koh, M. P.; Loh, Y. F. Fortification
398 of sulfited tannin from the bark of Acacia mangium with phenol-formaldehyde for use
399 as plywood adhesive. *Industrial Crops and Products*, **2009**, 30(3), 416-421.
400 DOI:10.1016/j.indcrop.2009.07.012.

401 [9] Moubarik, A.; Pizzi, A.; Allal, A.; Charrier, F.; Charrier, B. Cornstarch and tannin
402 in phenol-formaldehyde resins for plywood production. *Industrial Crops and*
403 *Products*, **2009**, 30(2), 188-193. DOI: 10.1016/j.indcrop.2009.03.005.

404 [10] Li, J.; Zhu, W. ; Zhang, S. ; Gao, Q. ; Xia, C. ; Zhang, W. ; Li, J.
405 Depolymerization and characterization of Acacia mangium tannin for the preparation
406 of mussel-inspired fast-curing tannin-based phenolic resins. *Chemical Engineering*
407 *Journal*, **2019**, 370, 420-431. DOI:10.1016/j.cej.2019.03.211.

408 [11] Yue, L.; Shi, R.; Yi, Z.; Shi, S. Q.; Gao, Q.; Li, J. A high-performance soybean
409 meal-based plywood adhesive prepared via an ultrasonic process and using
410 significantly lower amounts of chemical additives. *Journal of Cleaner Production*,
411 **2020**, 274, 123017. DOI: 10.1016/j.jclepro.2020.123017.

412 [12] Xu, Y.; Xu, Y.; Zhu, W.; Zhang, W.; Gao, Q.; Li, J. Improve the performance of
413 soy protein-based adhesives by a polyurethane elastomer. *Polymers*, **2018**, 10(9),

414 1016. DOI: 10.3390/polym10091016.

415 [13]Chen, M.; Luo, J.; Shi, R.; Zhang, J.; Gao, Q.; Li, J. Improved adhesion
416 performance of soy protein-based adhesives with a larch tannin-based resin. *Polymers*,
417 **2017**, 9(9), 408. DOI: 10.3390/polym9090408.

418 [14]Wang, Z.; Zhu, H.; Huang, J.; Ge, Z.; Guo, J.; Feng, X.; Xu, Q. Improvement of
419 the bonding properties of cassava starch-based wood adhesives by using different
420 types of acrylic ester. *International journal of biological macromolecules*, **2019**, 126,
421 603-611. DOI: 10.1016/j.ijbiomac.2018.12.113.

422 [15]Li, P.; Wu, Y.; Zhou, Y.; Zuo, Y. Preparation and characterization of
423 resorcinol-dialdehyde starch-formaldehyde copolycondensation resin adhesive.
424 *International journal of biological macromolecules*, **2019**, 127, 12-17. DOI:
425 10.1016/j.ijbiomac.2018.12.249.

426 [16]Jiang, W.; Kumar, A.; Adamopoulos, S. Liquefaction of lignocellulosic materials
427 and its applications in wood adhesives-A review. *Industrial Crops and Products*, **2018**,
428 124, 325-342. DOI: 10.1016/j.indcrop.2018.07.053.

429 [17]Alma, M. H.; Basturk, M. A. Liquefaction of grapevine cane (*Vitis vinisera* L.)
430 waste and its application to phenol–formaldehyde type adhesive. *Industrial crops and*
431 *products*, **2006**, 24(2), 171-176. DOI: 10.1016/j.indcrop.2006.03.010.

432 [18]Alma, M. H.; Baştürk, M. A.; Shiraishi, N. Cocondensation of NaOH-catalyzed
433 liquefied wood wastes, phenol, and formaldehyde for the production of resol-type
434 adhesives. *Industrial & engineering chemistry research*, **2001**, 40(22), 5036-5039.
435 DOI: 10.1021/ie000858x.

-
- 436 [19]Shirmohammadli, Y.; Efhamisisi, D.; Pizzi, A. Tannins as a sustainable raw
437 material for green chemistry: A review. *Industrial Crops and Products*, **2018**, 126,
438 316-332. DOI:10.1016/j.indcrop.2018.10.034.
- 439 [20]Liu, J.; Wang, L.; Li, J.; Li, C.; Zhang, S.; Gao, Q.; Zhang, W.; Li, J. Degradation
440 mechanism of Acacia mangium tannin in NaOH/urea aqueous solution and
441 application of degradation products in phenolic adhesives. *International Journal of*
442 *Adhesion and Adhesives*, **2020**, 98, 102556. DOI: 10.1016/j.ijadhadh.2020.102556.
- 443 [21]Pizzi, A. Recent developments in eco-efficient bio-based adhesives for wood
444 bonding: opportunities and issues. *Journal of adhesion science and technology*, **2006**,
445 20(8), 829-846. DOI:10.1163/156856106777638635.
- 446 [22]Kamoun, C.; Pizzi, A. Mechanism of hexamine as a non-aldehyde
447 polycondensation resins hardener. Part 1: Hexamine decomposition and reactive
448 intermediates. *Holzforschung und Holzverwertung*, **2000**, 52(1), 16-19.
- 449 [23]Efhamisisi, D. ; Thevenon, M. F. ; Hamzeh, Y. ; Karimi, A. N. ; Pizzi, A. ;
450 Pourtahmasi, K. Induced tannin adhesive by boric acid addition and its effect on
451 bonding quality and biological performance of poplar plywood. *ACS Sustainable*
452 *Chemistry & Engineering*, **2016**, 4(5), 2734-2740. DOI:
453 10.1021/acssuschemeng.6b00230.
- 454 [24]Ballerini, A.; Despres, A. ; Pizzi, A. Non-toxic, zero emission tannin-glyoxal
455 adhesives for wood panels. *Holz als Roh-und Werkstoff*, **2005**, 63(6), 477-478. DOI:
456 10.1007/s00107-005-0048-x.
- 457 [25]Zhang, J.; Xi, X. ; Liang, J. ; Pizzi, A. ; Du, G. ; Deng, S. Tannin-based adhesive

458 cross-linked by furfuryl alcohol-glyoxal and epoxy resins. *International Journal of*
459 *Adhesion and Adhesives*, **2019**, 94, 47-52. DOI: 10.1016/j.ijadhadh.2019.04.012.

460 [26]Zhou, X.; Pizzi, A. Pine tannin based adhesive mixes for plywood. *International*
461 *Wood Products Journal*, **2014**, 5(1), 27-32. DOI: 10.1179/204264531Y.00000000043.

462 [27]Faris, A. H.; Rahim, A. A.; Ibrahim, M. N. M.; Alkurdi, A. M.; Shah, I.
463 Combination of lignin polyol-tannin adhesives and polyethylenimine for the
464 preparation of green water- resistant adhesives. *Journal of Applied Polymer Science*,
465 **2016**, 133(20), 43437. DOI: 10.1002/app.43437.

466 [28]Xi, X.; Pizzi, A.; Frihart, C.; Lorenz, L.; Gerardin, C. Tannin plywood
467 bioadhesives with non-volatile aldehydes generation by specific oxidation of
468 mono-and disaccharides. *International Journal of Adhesion and Adhesives*, **2020**, 98,
469 102499. DOI: 10.1016/j.ijadhadh.2019.102499.

470 [29]Navarrete, P.; Pizzi, A.; Tapin-Lingua, S.; Benjelloun-Mlayah, B.; Pasch, H.;
471 Rode, K.; Delmotte, L.; Rigolet, S. Low formaldehyde emitting biobased wood
472 adhesives manufactured from mixtures of tannin and glyoxylated lignin. *Journal of*
473 *Adhesion Science and Technology*, **2012**, 26(10-11), 1667-1684. DOI:
474 10.1163/156856111X618489.

475 [30]Ping, L.; Gambier, F.; Pizzi, A.; Guo, Z. D.; Brosse, N. Wood adhesives from
476 agricultural by-products: Lignins and tannins for the elaboration of particleboards.
477 *Cellulose Chem. Technol*, **2012**, 46(7-8), 457-462.

478 [31]Ghahri, S.; Pizzi, A.; Mohebby, B.; Mirshokraie, A.; Mansouri, H. R. Soy-based,
479 tannin-modified plywood adhesives. *The Journal of Adhesion*, **2018**, 94(3), 218-237.

480 DOI: 10.1080/00218464.2016.1258310.

481 [32]Laigle, Y.; Kamoun, C.; Pizzi, A. Particleboard IB forecast by TMA bending in UF
482 adhesives curing. *European Journal of Wood and Wood Products*, **1998**, 56(3),
483 154-154. DOI: 10.1007/s001070050288.

484 [33]Xi, X.; Liao, J.; Pizzi, A.; Gerardin, C.; Amirou, S.; Delmotte, L.
485 5-Hydroxymethyl furfural modified melamine glyoxal resin. *The Journal of Adhesion*,
486 **2019**, 1-19. DOI: 10.1080/00218464.2018.1561291.

487 [34]Chen, X.; Li, J.; Xi, X.; Pizzi, A.; Zhou, X.; Fredon, E.; Du, G. ; Gerardin, C.
488 Condensed tannin-glucose-based NIPU bio-foams of improved fire retardancy.
489 *Polymer Degradation and Stability*, **2020**, 175, 109121. DOI:
490 10.1016/j.polymdegradstab.2020.109121 (2020).

491 [35]Luo, J.; Zhou, Y.; Gao, Q.; Li, J.; Yan, N. From wastes to functions: A new
492 soybean meal and bark-based adhesive. *ACS Sustainable Chemistry & Engineering*,
493 **2020**, 8(29), 10767-10773. DOI: 10.1021/acssuschemeng.0c02413.

494 [36]Chen, X. ; Xi, X. ; Pizzi, A. ; Fredon, E. ; Zhou, X. ; Li, J. ; Gerardin, C. ; Du, G.
495 Preparation and Characterization of Condensed Tannin Non-Isocyanate Polyurethane
496 (NIPU) Rigid Foams by Ambient Temperature Blowing. *Polymers*, **2020**, 12(4), 750.
497 DOI: 10.3390/polym12040750.

498 [37]Li, J.; Luo, J.; Li, X.; Yi, Z.; Gao, Q.; Li, J. Soybean meal-based wood adhesive
499 enhanced by ethylene glycol diglycidyl ether and diethylenetriamine. *Industrial Crops
500 and Products*, **2015**, 74, 613-618. DOI: 10.1016/j.indcrop.2015.05.066.

501 [38]Luo, J.; Li, C.; Li, X.; Luo, J.; Gao, Q.; Li, J. A new soybean meal-based

502 bioadhesive enhanced with 5, 5-dimethyl hydantoin polyepoxide for the improved
503 water resistance of plywood. *RSC Advances*, **2015**, 5(77), 62957-62965. DOI:
504 10.1039/C5RA05037E.

505 [39]Ferdosian, F.; Yuan, Z.; Anderson, M.; Xu, C.C. Synthesis and characterization of
506 hydrolysis lignin-based epoxy resins. *Industrial Crops and Products*, **2016**, 91,
507 295-301. DOI:10.1016/j.indcrop.2016.07.020.

508 [40]Younesi-Kordkheili, H.; Pizzi, A. (2020). Improving the properties of
509 urea-lignin-glyoxal resin as a wood adhesive by small addition of epoxy. *International*
510 *Journal of Adhesion and Adhesives*, **2020**, 102, 102681.
511 doi:10.1016/j.ijadhadh.2020.102681.

512 [41]Xin, J.; Li, M.; Li, R.; Wolcott, M. P.; Zhang, J. Green Epoxy Resin System
513 Based on Lignin and Tung Oil and Its Application in Epoxy Asphalt. *ACS Sustainable*
514 *Chemistry & Engineering*, **2016**, 4, 2754-2761.
515 DOI:10.1021/acssuschemeng.6b00256.

516 [42]Jahanshahi, S.; Pizzi, A.; Abdulkhani, A.; Shakeri, A. Analysis and testing of
517 bisphenol A-Free bio-based tannin epoxy-acrylic adhesives. *Polymers*, **2016**, 8(4), 143.
518 DOI: 10.3390/polym8040143.

519 [43]Zhang, S.; Liu, T.; Hao, C.; Wang, L.; Han, J.; Liu, H.; Zhang, J. Preparation of a
520 lignin-based vitrimer material and its potential use for recoverable adhesives. *Green*
521 *Chemistry*, **2018**, 20(13), 2995-3000. DOI: 10.1039/c8gc01299g.

522 [44] Jahanshahi, S.; Pizzi, A.; Abdulkhani, A.; Doosthoseini, K.; Shakeri, A.; Lagel, M.
523 C.; Delmotte, L. MALDI-TOF, ¹³C NMR and FT-MIR analysis and strength

524 characterization of glycidyl ether tannin epoxy resins. *Industrial Crops and Products*,
525 **2016**, 83, 177-185. DOI:10.1016/j.indcrop.2015.11.067.

526 [45]Pasch, H.; Pizzi, A.; Rode, K. MALDI-TOF mass spectrometry of polyflavonoid
527 tannins. *Polymer*, **2001**, 42(18), 7531-7539. DOI: 10.1016/S0032-3861(01)00216-6.

528 [46]Abdalla, S.; Pizzi, A.; Ayed, N.; Charrier, F.; Bahabri, F.; Ganash, A.
529 MALDI-TOF and ¹³C NMR analysis of Tunisian Zizyphus jujuba root bark tannins.
530 *Industrial Crops and Products*, **2014**, 59, 277-281.
531 DOI:10.1016/j.indcrop.2014.05.035.

532 [47]Pizzi, A. *Advanced wood adhesives technology*; CRC Press: New York, 1994.

533 [48]Nicollin, A.; Zhou, X.; Pizzi, A.; Grigsby, W.; Rode, K.; Delmotte, L.
534 MALDI-TOF and ¹³C NMR analysis of a renewable resource additive-Thermoplastic
535 acetylated tannins. *Industrial crops and products*, **2013**, 49, 851-857. DOI:
536 10.1016/j.indcrop.2013.06.013.

537 [49]Pizzi, A.; Stephanou, A. A comparative ¹³C NMR study of polyflavonoid tannin
538 extracts for phenolic polycondensates. *Journal of applied polymer science*, **1993**,
539 50(12), 2105-2113. DOI: 10.1002/app.1993.070501209.

540 [50]Navarrete, P.; Pizzi, A.; Bertaud, F; Rigolet, S. Condensed tannin reactivity
541 inhibition by internal rearrangements: Detection by CP-MAS ¹³C NMR. *Maderas:*
542 *Ciencia y tecnología*, **2011**, 13(1), 59-68. DOI: 10.4067/S0718-221X2011000100006.