

Hydroxymethylfurfural Hardening of Pine Tannin Wood Adhesives

F.-J. Santiago-Medina¹, A. Pizzi^{1,2,*} and S. Abdalla²

¹LERMAB, 27 rue Philippe Seguin, BP 1041 88051 Epinal cedex 9, France

²Department of Physics, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Received August 19, 2017; Accepted September 11, 2017

ABSTRACT An adhesive based on the reaction of a very fast reacting procyanidin-type condensed tannin, namely purified pine bark tannin, with a biosourced nontoxic and nonvolatile aldehyde derived from the pulp and paper industry, namely hydroxymethylfurfural (HMF), was shown to almost satisfy the relevant standards for bonding wood particleboard. The conditions of pH used are determinant for the result. The oligomers obtained by the reaction and their distribution have been determined by matrix-assisted laser ionization desorption time-of-flight (MALDI-TOF) mass spectrometry. Of the two reactive groups of hydroxymethylfurfural capable of reacting, the furanic aldehyde one and the furanic hydroxymethyl alcohol group, only the first one appears to mainly react, the second one reacting minimally or not at all under the alkaline conditions used.

KEYWORDS Wood adhesives, pine tannin, hydroxymethylfurfural, MALDI-TOF

1 INTRODUCTION

Tannin-based wood panel adhesives have now been commercialized for a long time [1–3]. Their technology is based on their crosslinking and hardening with formaldehyde [2, 4]. As stricter regulations on formaldehyde use and emission have been implemented, alternative routes for hardening these natural adhesives have been sought. Among these are: (i) the use of nontoxic, nonvolatile aldehydes, such as glyoxal [5, 6, 7], and other biosourced ones, such as vanillin and derivatives [8], although these work only with the more reactive procyanidin-type condensed tannins such as pine tannins; (ii) the condensation of tannins with furfuryl alcohol [7, 9]; (iii) the condensation of tannins with triethyl phosphate [10]; and (iv) the condensation of tannins with ammonia and diamines and polyamines [11, 12]. Not all these technologies are adaptable for use for wood panel binders. Thus, (iii) and (iv) above are effective for higher temperature curing, not for wood panels.

While alternative aldehydes constitute an interesting approach [2, 13, 14], when they are inexpensive, they always present the drawback of having a lower

reactivity than formaldehyde. Thus, their use is limited to procyanidin-type tannins, the more reactive of the condensed flavonoid tannins. Among these, the more purified the tannin extract, the more reactive it is. Thus, pure procyanidin tannins from which any interfering carbohydrate fractions have been eliminated are more suitable for use with alternative aldehydes, as already shown for the reaction with vanillin and its derivatives [8].

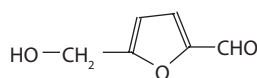
Hydroxymethylfurfural (HMF) is a biosourced aldehyde derivative of furan obtained by dehydration of three water molecules from hexose, which can be used as an intermediate of plastics, polymers and fuels [15]. It can be produced in a number of different ways from relatively inexpensive and abundant biosourced natural materials such as glucose, fructose and starch [15–29]. Its preparation has recently attracted considerable interest due to its applications in the preparation of a number of biosourced polymers [15]. For example, preparation of HMF by dehydration of fructose in concentrated solutions of carboxylic acids, such as acetic acid or formic acid, and in the presence of a solid acid [16] solves the problems of the poor selectivity of the reaction due to the formation of furanic polymers (humins), especially when strong mineral acids such as HCl are employed. This approach [16], for example, appears to also solve the drawbacks of the alternative recent

*Corresponding author: antonio.pizzi@univ-lorraine.fr

DOI: 10.7569/JRM.2017.634166

methods which describe the use of toxic organic solvents to extract HMF and/or complex reaction mixtures (ionic liquid or concentrated solutions of transition metallic salts) to get high selectivities in 5-HMF preparation [17–29].

The interest of HMF lies in the existence of two reactive functions: the aldehyde itself and a highly reactive hydroxymethyl group on the furan ring (I).



Thus, HMF can react as furfural with its aldehyde group as well as reacting as furfuryl alcohol with its hydroxymethyl group. The aldehyde group is much less reactive than formaldehyde [2, 13]. Conversely, the hydroxymethyl group is highly reactive with tannins under very alkaline and especially very acid conditions [9]. However, the acid conditions under which its reaction is particularly fast are unsuitable for wood bonding as the strong residual acid in the cured glue line would cause hydrolysis and degradation of cellulose and hemicelluloses of the substrate, eventually impairing the mechanical resistance of the bonded joint. Systems of self-neutralization of very acid-setting phenolic resins [30], such as tannins, have been developed, but if the harsh acid curing conditions can be totally avoided the situation would be more acceptable. It is then necessary to use conditions that are less favorable for wood panels than the hydroxymethyl group, which makes it necessary to increase the reactivity of the other reagent involved, namely the tannin itself.

This study examines the hardening of purified, carbohydrate-free pine bark tannin with hydroxymethylfurfural under neutral and relatively mild alkaline conditions without using systems of self-neutralization for very acid-setting adhesives [30]. The reaction is then studied by determining the main oligomers formed and their distribution by the reaction of purified pine tannin with HMF, as well as testing the system as a bioadhesive for wood panels.

2 EXPERIMENTAL

Purified maritime pine (*Pinus pinaster*) bark tannin extract (Phenopyn) was obtained by DRT (Derives Resiniques et Terpeniques, Dax, France). It is a commercial product purified for use as food additive where the carbohydrates have been eliminated, leaving exclusively the polyphenolic part of the flavonoid, procyanidin-type tannin [31].

Hydroxymethylfurfural was obtained from Sigma-Aldrich (Saint Louis, Missouri, USA). The reaction of pine tannin with HMF was carried out under two different pHs, namely:

- i. To 1 g of an aqueous solution of pine tannin (containing 42% of solid) at pH 6.5 was added HMF (hydroxymethylfurfural) in the following proportion by weight, tannin solid:HMF solid of 5:1. The mixture was cured during four hours in an oven at 100 °C.
- ii. To 1 g of an aqueous solution of pine tannin (containing 42% of solid) at pH 9.5 was added HMF (hydroxymethylfurfural) in the following proportion by weight, tannin solid:HMF solid of 5:1. The mixture was cured during four hours in an oven at 100 °C.

2.1 MALDI-TOF Analysis

2.1.1 MALDI-TOF Mass Spectrometry

The spectra were recorded on a Kratos AXIMA Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical, Shimadzu Europe Ltd., Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. Measurements were carried out using the following conditions: polarity – positive, flight path – linear, 20 kV acceleration voltages, 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns. MALDI-MS software was used for the data treatment.

2.1.2 MALDI-TOF Sample Preparation

The samples were dissolved in a solution of water/acetone (1:1) up to 7.5 mg/ml. For the enhancement of ion formation NaCl solution was added and placed on the MALDI target. The solutions of the samples and the matrix were mixed in equal amounts and 1.5 µl of the resulting solution was placed on the MALDI target. As the matrix, 2,5-dihydroxy benzoic acid was used. Red phosphorous was used as reference for spectrum calibration. Finally, after evaporation of the solvent, the MALDI target was introduced into the spectrometer. Due to the addition of sodium salt in the positive mode, the majority of the mass peaks correspond to $[M+Na^+]$. In order to obtain the molecular weight of the chemical species of the peak, 23 Da for sodium must be subtracted where indicated in the tables.

2.2 Thermomechanical Analysis (TMA)

The experimental pine tannin/HMF adhesive systems were tested by thermomechanical analysis at 2 different pHs, namely 7.5 and 9.5, in a proportion of tannin solids to HMF solids of 5:1 by weight. The samples were prepared by applying each resin system between two beech wood plies in a layer of 350 μm , for total sample dimensions of $21 \times 6 \times 1.1$ mm. These beech-resin-beech specimens were tested in non-isothermal mode between 40 °C and 220 °C at a heating ratio of 10 °C/minute with Mettler Toledo 40 TMA equipment in three-point bending on a span of 18 mm, exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 seconds (6s/6s). The classical mechanics relationship between force and deflection

$$E = [L^3/(4bh^3)][\Delta F/(\Delta f_{\text{wood}} - \Delta f_{\text{adhesive}})]$$

allows the calculation of the Young's modulus E for each case tested. Such a measuring system has been introduced and is used to follow the progressive hardening of the adhesive with the increase of temperature and to indicate comparatively if an adhesive system is faster or slower hardening and if it gives stronger joints than another one [32–35].

2.3 Wood Particleboard Preparation and Testing

Duplicate identical monolayer particleboards were prepared using the following glue mix: 100 g of purified maritime pine (*Pinus pinaster*) tannin was dissolved in water to yield a concentration of 40–45% solids. The pH was corrected to 6.5 and 9.5 with NaOH solution at 33% concentration. To this was added 20 g (20% solids on solids) of HMF. The glue mix was applied at a level of 10% solids on dry industrial wood chips and the panels hot pressed at 220 °C for 7.5 minutes with a pressure cycle of 28 kg cm^{-3} /15 kg cm^{-3} /5 kg cm^{-3} for 2 min/2.5 min/3 min. After cooling, each panel was cut and 5 samples for each were tested for dry internal bond (IB) strength according to European Norm EN319, 1993 [36].

2.4 Gelation Time Test

The gel test for a tannin resin was performed as follows: 10 g of the reaction mixture composed of pine tannin as a 45% water solution to which HMF has been added in proportion by weight tannin solids:HMF = 5:1 solution were placed in a test tube and this was

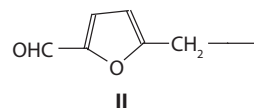
placed in a water bath, maintained at boiling temperature (100 °C) at normal atmospheric pressure. A wire spring was inserted in the test tube and rapidly moved up and down and the time to gelling was measured by stopwatch. The test was done in duplicate and the average value was reported.

This test is a standard FESYP (European Federation of Panels Manufacturers) test and is used extensively in Europe for wood adhesives [37].

3 RESULTS AND DISCUSSION

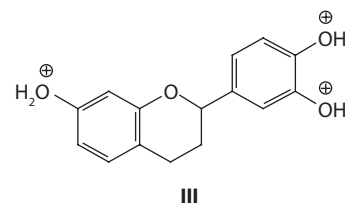
3.1 MALDI-TOF Analysis

For the sample reacted at pH 6.5 and 100 °C, a trend of peaks with a difference of 131–132 Da is noticed (Figures 1a–d). These are 701 Da, 833 Da, 964 Da, 1096 Da, 1228 Da, 1360 Da, 1498 Da, 1613 Da, 1755 Da, 1887 Da and 2019 Da. This trend can be assigned to a bonded HMF molecule plus Na (it means 126 Da-18+23 = 131 Da). Thus, HMF moieties of kind (II)



are progressively linked to the flavonoids of the oligomers formed by condensation of HMF and pine tannin.

The repeating period of 131 Da in maritime pine tannin has already been shown [31] to belong to a multi-protonated species in which an -OH, possibly the one linked in C3, has been lost either in the tannin extraction procedure or in the MALDI analysis, to form a $(131-132) \times 2 = 262-264$ Da species of the type (III).



Most of the peaks found at pH 9.5 present the same trend as for the case at pH 6.5.

In Tables 1 and 2 and Figures 1a–d one can notice dimers linked through two flavonoids having reacted with the aldehyde function of HMF as is the case for the species at 688 Da, a dimer found in both the reaction products at pH 6.5 and 9.5 (IV)

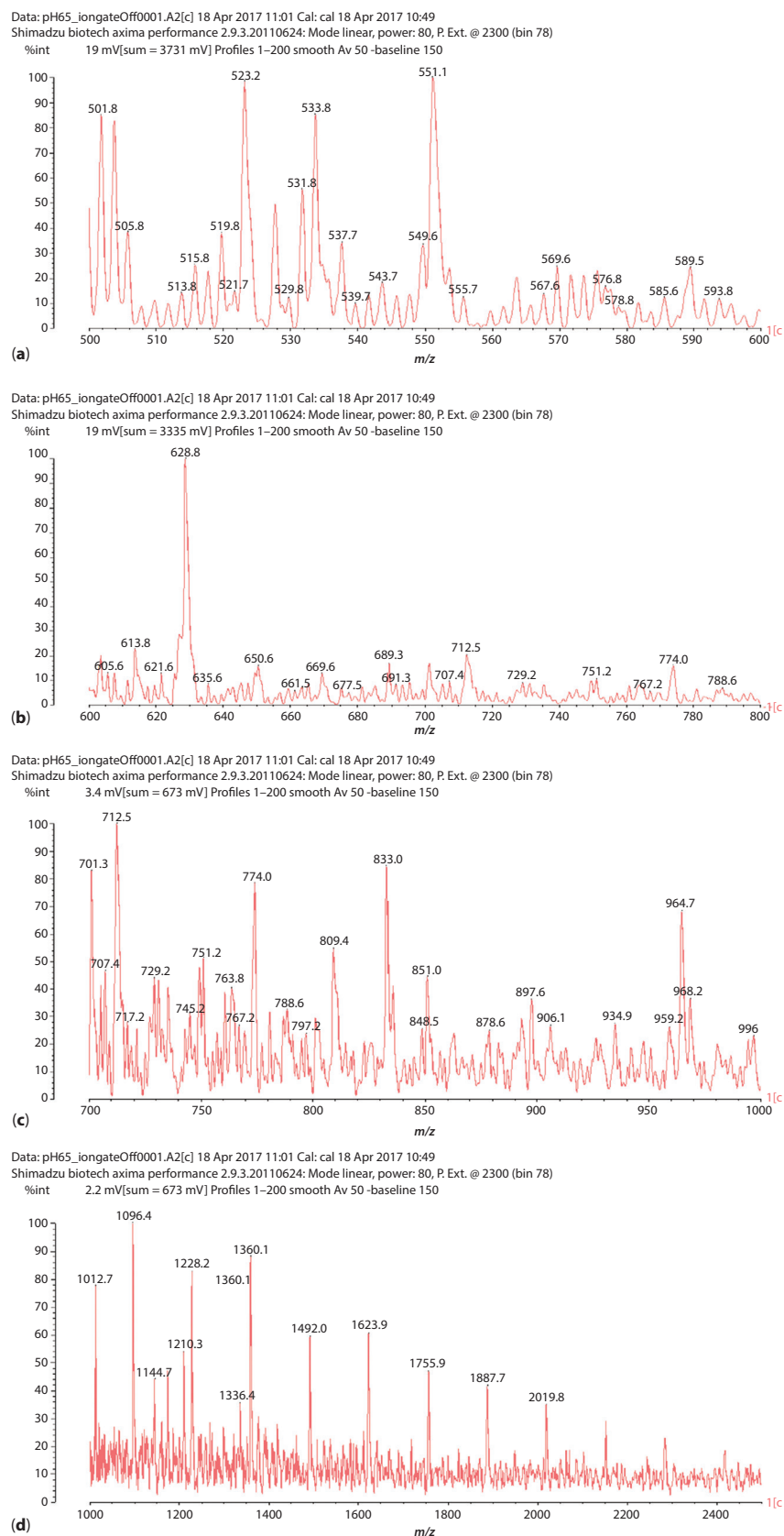


Figure 1 MALDI-TOF spectrum of the reaction of purified pine tannin with HMF at pH 6.5 and 100 °C: (a) 500 Da–600 Da range, (b) 600 Da–800 Da range, (c) 700 Da–1000 Da range, and (d) 1000 Da–2500 Da range.

Table 1 Maldi-TOF spectra interpretation of samples obtained by the reaction at pH 6.5 of pine tannin with HMF.

Experimental Mass	Calculated Mass	Type	Units of HMF ^a	Unit type					Na+
				264 Da	274 Da	290 Da	306 Da	442 Da	Yes/No
274	274	Monomer			1				No
306.4	306	Monomer					1		No
313.4	313	Monomer				1			Yes
330.4	329	Monomer					1		Yes
381.9	382	Monomer	1		1				No
442	442	Monomer						1	No
465.9	465	Monomer						1	Yes
513.8	513	Monomer	2		1				Yes
515.8	514	Monomer	2		1				Yes, protonated
523.2	524	Dimer		2					No
537.7	536	Dimer		1	1				No
549.6	549	Dimer		2					Yes
551.1	550	Monomer	1					1	No
	552	Dimer		1		1			No
567.6	568	Dimer		1			1		No
569.6	569	Dimer			2				Yes
578.8	578	Dimer				2			No
585.6	585	Dimer			1	1			Yes
593.8	594	Dimer				1	1		No
613.8	614	Monomer	3			1			No
621.8	621	Monomer	3		1				Yes
628.8	630	Monomer	3				1		No
635.6	635	Dimer	1	2					No
661.5	662	Dimer	1	1		1			No
669.6	668	Dimer	1	1	1				Yes
	670	Dimer	1		1	1			No
677.5	678	Dimer	1	1			1		No
	679	Dimer	1		2				Yes
689.3	688	Dimer	1		1		1		No
	688	Dimer	1			2			No
701	701	Dimer	1	1			1		Yes
707.4	706	Dimer	1	1		1			Yes (2)
712.5	714	Dimer			1			1	No
729.2	730	Dimer				1		1	No
774.0	771	Dimer					1	1	Yes
797.2	798	Trimer		2	1				No
788.6	788	Trimer		3					No
809.4	808	Trimer		1	2				No
833	834	Trimer			2	1			No
851	850	Trimer			2		1		No
	850	Trimer			1	2			No
878.6	879	Dimer	1				1	1	Yes

(Continued)

Table 1 Cont.

Experimental Mass	Calculated Mass	Type	Units of HMF ^a	Unit type					Na+
				264 Da	274 Da	290 Da	306 Da	442 Da	Yes/No
897.6	898	Trimer				1	2		No
906.1	905	Dimer						2	Yes
	905	Trimer				2	1		Yes
	905	Trimer			1		2		Yes
959.2	961								No
964.7	964		1		2		1		No
1096.4	1093	Trimer	2		2		1		Yes
	1093	Trimer	2		1	2			Yes
1144.7	1141	Trimer	2			1	2		Yes
	1144	Trimer		1				2	No
1210.3	1209	Trimer					1	2	Yes
	1209	Trimer	2	2				1	Yes
1228.2	1229	Trimer	2		2			1	Yes
1492.0	1490	Tetramer	3	1		1	2		No
	1491	Tetramer	3		1	3			Yes
	1491	Tetramer	3		2	1	1		Yes
1623.9	1623	Tetramer	3	2			1	1	Yes
	1626	Tetramer	3	1		1	1	1	No

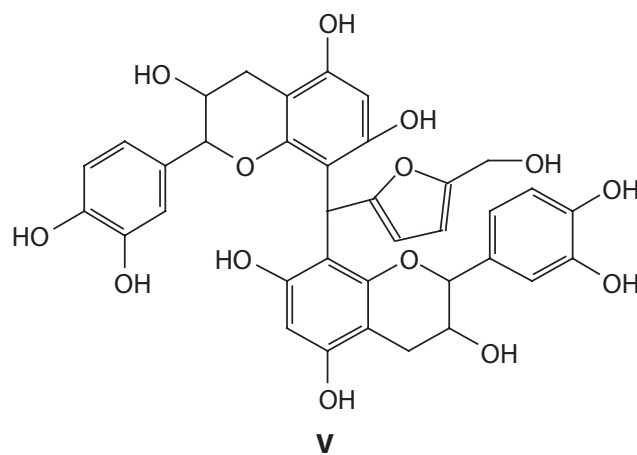
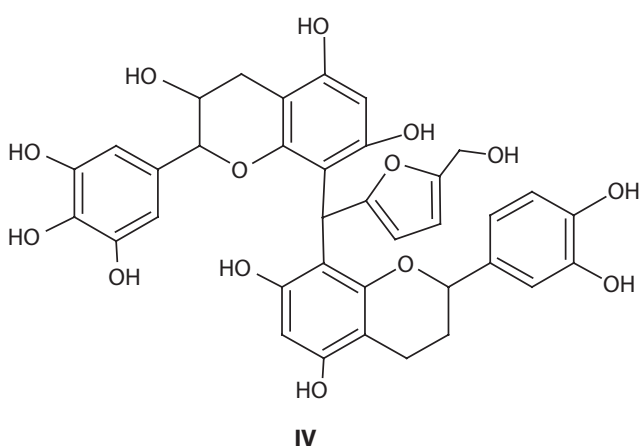
^aHMF= Hydroxymethylfurfural**Table 2** Maldi-TOF spectra interpretation of samples obtained by the reaction at pH 9.5 of pine tannin with HMF.

Experimental Mass	Calculated Mass	Type	Units of HMF	Unit type					Na+
				264 Da	274 Da	290 Da	306 Da	442 Da	Yes/No
264	264	Monomer		1					No
274,4	274	Monomer			1				No
298	297	Monomer			1				Yes
306,4	306	Monomer					1		No
330,3	329	Monomer					1		Yes
382,1	382	Monomer	1		1				No
414,1	414	Monomer	1				1		No
421,2	422	Monomer	1			1			Yes
442	442	Monomer						1	No
465,9	465	Monomer						1	Yes
527,8	526	Dimer		2					No
537,8	536	Dimer		1	1				No
549,7	549	Dimer		2					Yes
551,3	550	Monomer	1					1	No
	552	Dimer		1		1			No
563,7	562	Dimer			1	1			No
567,7	568	Dimer		1			1		No

(Continued)

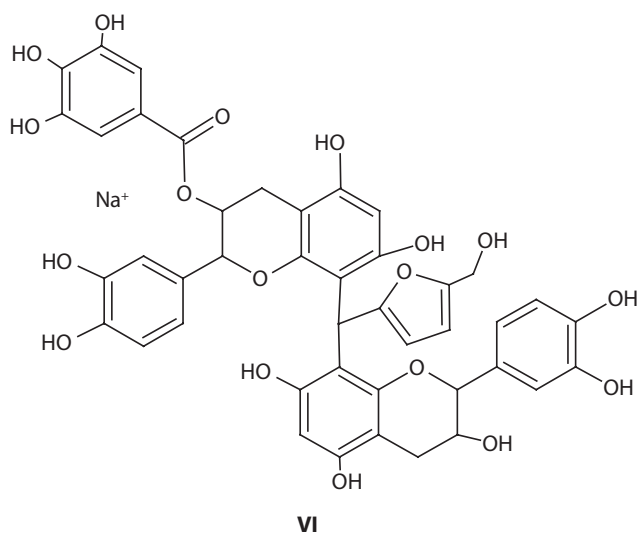
Table 2 Cont.

Experimental Mass	Calculated Mass	Type	Units of HMF	Unit type					Na+
				264 Da	274 Da	290 Da	306 Da	442 Da	Yes/No
573,7	573	Monomer	1					1	Yes
	574	Monomer	1					1	Yes
575,6	575	Dimer		1		1			Yes
595,6	594	Dimer				1	1		No
	597	Monomer	1					1	Yes (2)
617,5	617	Dimer				1	1		Yes
669,8	668	Dimer	1	1	1				Yes
	669	Dimer	1	1	1				Yes
	671	Dimer	1		1	1			No
689,4	688	Dimer	1			2			No
	688	Dimer	1		1		1		No
712,4	711	Dimer	1			2			Yes
	711	Dimer	1		1		1		Yes
729,2	730	Dimer				1		1	No
788,6	788	Trimer		3					No
809,9	808	Trimer		1	2				No
833,4	830	Trimer		1			1		No
	834	Trimer			2	1			No
851,3	850	Trimer			2		1		No
	850	Trimer			1	2			No
862,6	863	Trimer		1	2				Yes
	863	Dimer	1			1		1	Yes
867,1	866	Trimer				3			No

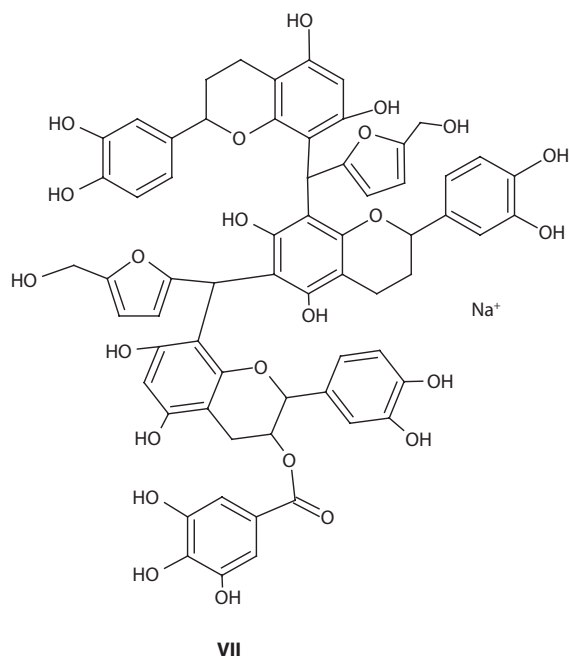


or its equivalent and more probable alternative for a mainly procyanidin tannin not having lost the -OH in C3 (V).

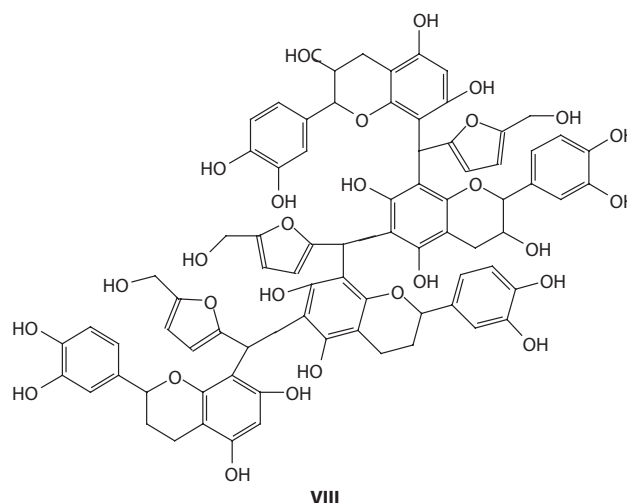
The existence of catechin gallate species in maritime pine tannin has already been shown [31]. This species also react to form oligomers such as shown by the dimer found only at pH 9 (Table 2) at 863 Da (VI).



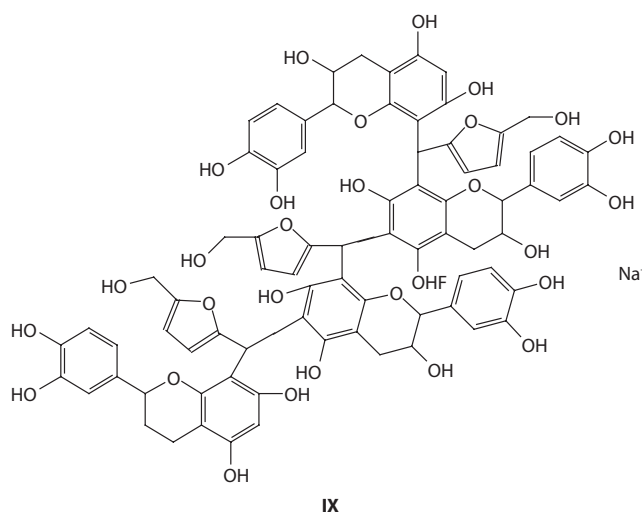
The possibility of a loss of an $-OH$ either in extraction or most probably in the MALDI analysis is exemplified by structures such as those of 1228-1229 Da. In this structure, two flavonoids of molecular weight 274 Da are present, 274 Da being in general a fisetinidin. However, in procyanidin tannins, while some fisetinidin is present, this is unlikely to be in any major proportions [31]. Thus, one can envisage the possibility that the oligomer at 1228-1229 Da presents either two fisetinidins in its structure or two catechin units having lost one $-OH$ group as is the case of structure (A) above. The 1228-1229 Da species, found both at pH 6.5 and pH 9.5, can then be either represented as (VII)



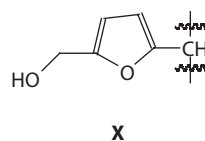
or with two fisetinidins. The same applies, for example, to the tetramer at 1453 Da found in the products of the reaction at pH 9.5 (VIII)



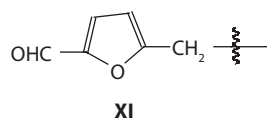
and in the tetramer at 1492 Da found both at pH 6.5 and 9.5 (IX).



However, reaction of pure pine tannin with HMF also gives a different dimension to some of the series of peaks obtained by MALDI-TOF. Thus, for the sample reacted at pH 6.5 and 100 °C, a trend of peaks with repeating period difference of 131-132 Da is noticed. These are 701 Da, 833 Da, 964 Da, 1096 Da, 1228 Da, 1360 Da, 1498 Da, 1613 Da, 1755 Da, 1887 Da and 2019 Da. This trend can be assigned to a bonded HMF molecule plus Na (it means 126 Da-18+23 = 131 Da). Thus, HMF moieties of the kind of structures (X) and (XI)

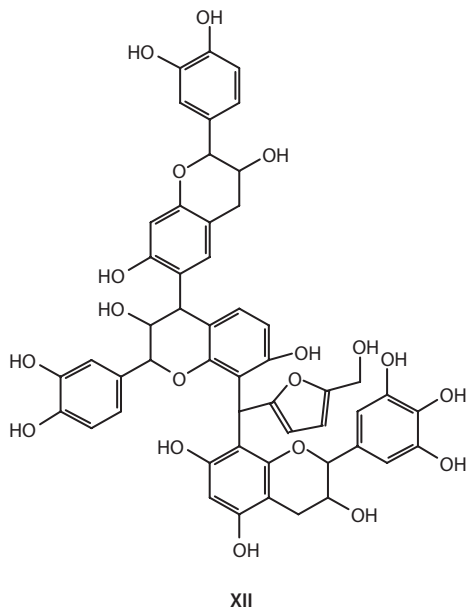


and/or



are progressively linked to the flavonoids of the oligomers formed by condensation of HMF and pine tannin. The lack at lower molecular weights of condensation products where the furanic hydroxymethyl group has reacted under the neutral and alkaline conditions used renders unlikely, or at least rather limits the presence of the second of these two groups to be attached as an appendix to the flavonoid. This, however, cannot be totally excluded.

The presence of peaks in which a defect of the first of these units is present indicates that tannin oligomers also react. Thus, the peaks at 959.2 Da and 964.7 Da can be interpreted as a non-protonated or protonated flavonoid dimer linked through a furfuraldehyde group with a non-protonated or protonated flavonoid monomer, for example, structure (XII).



While the peak at 1096.4 could be a multiprotonated form of either A or an equally multiprotonated but totally different trimer such as B (XIII).

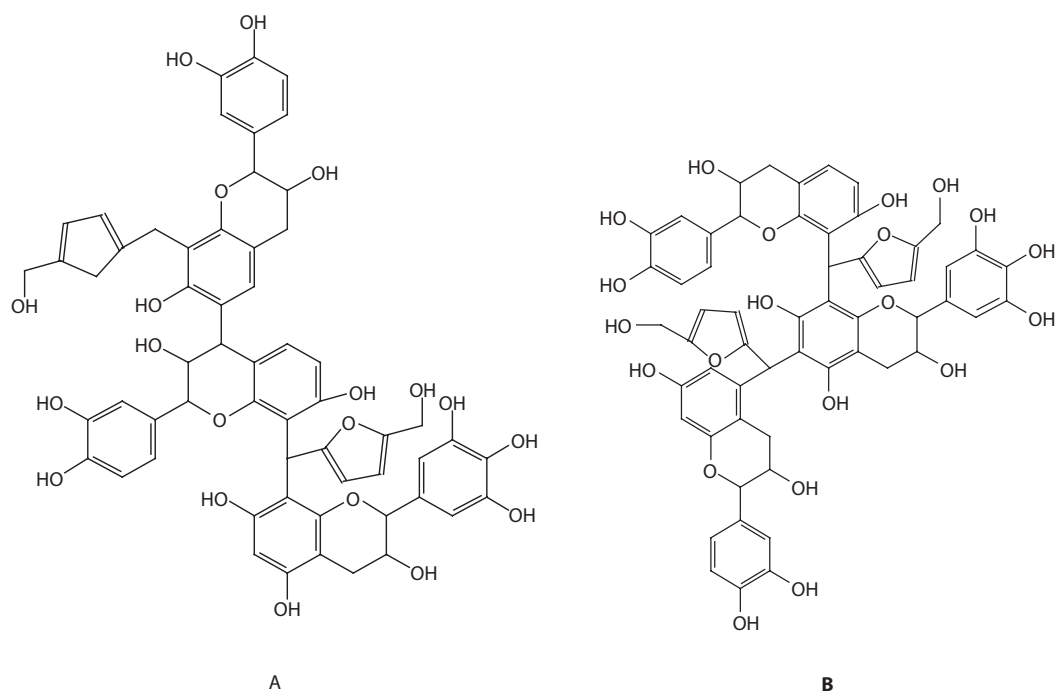
The same uncertainty applies for the higher peaks of the series, thus 1228 Da, 1360 Da, 1492 Da, 1623 Da, 1755 Da, 1887 Da and 2019 Da, as well as the three at 2151 Da, 2283 Da and 2415 Da, all separated by the 131-132 Da repeating period.

One point of interest is that the aldehyde function of HMF appears to react readily at 100 °C with the tannin. The reaction of furanic aldehyde groups with different tannins has already been reported for furfural [2, 13]. What is of greater interest is that the

hydroxymethyl group of HMF does not appear to react with the very reactive procyanidin tannin at 100 °C. In effect, the reaction of this group is favored by very acidic conditions, conditions that cannot be used for wood adhesives due to degradation of the lignocellulosic substrate induced by the acid, although self-neutralization systems to minimize such substrate degradation have been developed [30]. The furanic hydroxymethyl group, however, has been shown to react at alkaline pHs but at pHs higher than 7 with a much less reactive tannin than the one used here (mimosa tannin) [9]. This means that for the reaction at pH 6.5, while one would expect a slower reaction than that of the aldehyde group, the reaction with a fast procyanidin-type tannin as used here can possibly occur, but slower than the aldehyde group [2, 13]. The case is even stronger for both groups—the furanic aldehyde and hydroxymethyl group—to react with the tannin when the reaction is carried out at pH 9.5. The reason for this is that at the lower pH used the furanic hydroxymethyl group of furfuryl alcohol reacts rather slowly, which, while definitely valid for slower tannins [9], might not completely apply to the more reactive procyanidin-type tannins. There are then two effects contrary to each other; the lower reactivity or no reactivity of the furanic hydroxymethyl group countered by the higher reactivity of the type of tannin used. The results of hardening will depend on which of these two effects predominates. It can be seen later from the particleboard results that indeed the reaction may well be too fast at pH 9.5, causing early immobilization on hardening of the network and precluding complete crosslinking with consequences on the mechanical performance of the hardened adhesive (seen later). Instead, at pH 7.5 the reaction is not sufficiently fast and thus crosslinking occurs mainly by reaction of the aldehyde group of HMF and seemingly less or much less through the furanic hydroxymethyl group. The MALDI at 6.5 then has a pH too low to show participation of the hydroxymethyl group in crosslinking, hence the MALDI results where no participation of this group appears. At pH 9.5, early immobilization on hardening of the network precludes complete crosslinking with equally negative consequences on the mechanical performance of the hardened adhesive, this latter result being confirmed by the gel time results in Table 4.

3.2 Thermomechanical Analysis (TMA)

The results of the thermomechanical analysis are shown in Figures 2 and 3. The curve of the TMA for tannin alone in Figure 2 shows a single highest MOE value at a temperature of 150 °C, while the reaction of



XIII

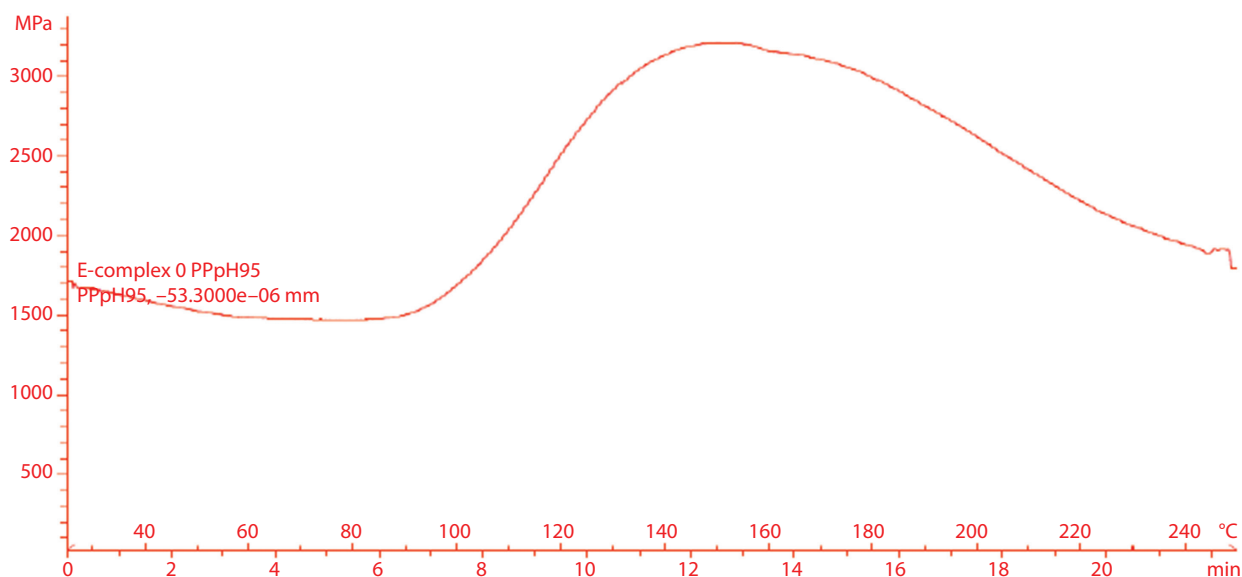


Figure 2 Thermomechanical analysis (TMA) of the self-condensation of purified pine tannin at pH 7.5 in the 40–220 °C range.

tannin with HMF shows two distinct peaks (Figure 3), namely one at 135 °C and a second one at 193 °C. It is difficult to assign to what these two peaks correspond. The lower temperature one most likely belongs to the reaction of the aldehyde group of HMF with the tannin, leading first to the kind of oligomers observed by MALDI-TOF and then to crosslinking. The higher temperature one is instead likely to correspond to the reaction of the hydroxymethyl group of HMF with the tannin. As shown by the type of oligomers observed by

MALDI, this group does not appear to react at lower temperatures with the tannin, and thus it is likely that the second peak leading to further crosslinking is due to its reaction. It is interesting to note that while the highest MOE value obtained with the tannin alone is a value of 3150 Mpa, in the case of the reaction of the pine tannin with the HMF the lower peak presents an MOE of 3700 MPa and the higher peak a value of 4200 MPa, both indicating two different crosslinking reactions.

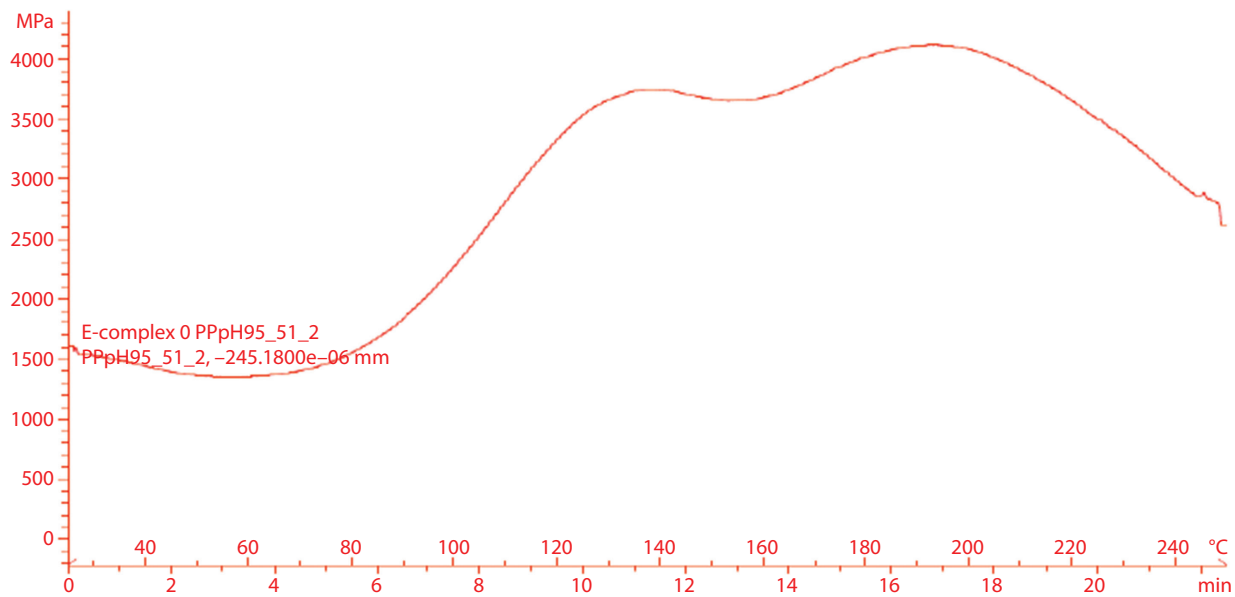


Figure 3 Thermomechanical analysis (TMA) of the condensation of purified pine tannin with HMF at pH 7.5 in the 40–220 °C range.

3.3 Particleboard Testing

The internal bond (IB) strength is the best measure of the effectiveness of bonding of an adhesive in particleboard. The results obtained are shown in Table 3. The IB strength obtained is lower than the requirements of the relevant standards (≥ 0.35 MPa). This is understandable, because at the press temperature used, characteristic of industrial applications, and at the percentage moisture content of the resinated particles the temperature in the core of a particleboard reaches 115–120 °C at most [38, 39]. As the IB strength depends exclusively on the strength of the board core, TMA and MALDI results indicate that the first reaction of crosslinking that is dependent on the reaction of the tannin with the aldehyde group of HMF only comes into play. This is evidently not enough to reach the IB strength required by the relevant standards. The temperature reached in the core is still too low to allow reaction of the furanic hydroxymethyl group under the alkaline conditions used. The situation is different in the board surfaces where the higher temperature reached, generally up to 180 °C, may well promote further crosslinking due to reaction of the furanic hydroxymethyl group of HMF. This may positively influence some board properties such as screw holding and bending strength. In particular, the need for higher temperature indicates that such tannin-HMF adhesive systems may be best suited to bond thin boards (3–6 mm thickness) as the temperatures reached in their core are generally higher. As regards the influence of pH on the reactions, both

Table 3 Average internal bond (IB) strength of laboratory particleboard panels bonded with pine tannin and HMF.

pH	IB strength (MPa)	Panel density (kg/m ³)
6.5–7.0	0.299	679
9.5	0.152	693

Table 4 Gel times at 100 °C of the pine tannin reaction with HMF in the proportion by weight of tannin solids:HMF = 5:1.

pH	Seconds
6.7	142 ± 3
9.5	38s ± 2s

the gel time at 100 °C (Table 4) and the board results indicate that the reaction is too fast at pH 9.5. This causes early immobilization on hardening of the network, precluding complete crosslinking. Thus, the mechanical performance of the hardened adhesive is lower. Instead, at pH 7.5 the reaction is not sufficiently fast (Tables 3 and 4) and thus crosslinking occurs mainly by reaction of the aldehyde group of HMF and seemingly less or much less through the furanic hydroxymethyl group. Optimization of the reaction, if not relying on just an increase in press temperature, might have to be optimized within a rather narrow range of pH.

It is difficult to compare the mechanical results we obtained with those reported by other authors. These authors have prepared phenol-HMF resins

but for glass fiber composites [40–42]. The only test vaguely comparable with ours is the bending strength obtained by DMA or TMA. Thus, the type of composite bending strengths reported in their tests is between 82 and 233 MPa [40, 41], and is around 800 MPa when the phenol-HMF and pyrolysis bio-oil-HMF are hardened with an epoxy resin [40, 41]. More comparable to the results obtained in this study, a range of bending modulus is reported for glass fiber composites bonded with a number of rather different phenol-HMF resins of between 2500 and 8700 MPa [42], whereas our results show a range of 3200 to 4200 MPa (Figures 2 and 3). It must be pointed out, however, that these glass fiber results reported are obtained with the aid of adding other reinforcing resins and catalysts [42], while the results in this study are by straight reaction between a natural phenol (tannin) and HMF. Furthermore, the work on glass fiber composites mentions extension of their patent application to cardanol and lignin, without any proof of the results with these, but not to tannin [42].

4 CONCLUSIONS

Wood panel adhesives based on the reaction under neutral pH conditions of a fast reacting procyanidin-type condensed tannin, namely purified pine bark tannin, with a biosourced nontoxic and non-volatile aldehyde, hydroxymethylfurfural (HMF), were shown to almost satisfy the relevant standards for bonding wood particleboard. The oligomers obtained by the reaction and their distribution have been determined by matrix-assisted laser ionization desorption time-of-flight (MALDI-TOF) mass spectrometry. Of the two reactive groups of hydroxymethylfurfural capable of reacting, the furanic aldehyde one and the furanic hydroxymethyl alcohol group, only the first one appears to mainly react under conditions predominant in the board core. The furanic hydroxymethyl alcohol group instead reacts minimally, or not at all, under the neutral or alkaline conditions used. Thermomechanical analysis has shown that this group starts to react only at higher temperature. A number and variety of oligomers formed by flavonoid monomers or dimers linked through HMF have been identified.

REFERENCES

1. A. Pizzi and H. Scharfetter, The chemistry and development of tannin-based wood adhesives for exterior plywood. *J. Appl. Polym. Sci.* **22**, 1745–1761 (1978).

2. A. Pizzi, *Wood Adhesives Chemistry and Technology*, Vol. 1, Marcel Dekker, New York (1983).
3. J. Valenzuela, E. von Leyser, A. Pizzi, C. Westermeyer, and B. Gorrini, Industrial production of pine tannin-bonded particleboard and MDF. *Eur. J. Wood Prod.* **70**, 735–740 (2012).
4. A. Pizzi, *Advanced Wood Adhesives Technology*, Marcel Dekker, New York (1994).
5. A. Ballerini, A. Despres, and A. Pizzi, Non-toxic, zero-emission tannin-glyoxal adhesives for wood panels. *Holz Roh Werkst.* **63**, 477–478 (2005).
6. P. Navarrete, H.R. Mansouri, A. Pizzi, S. Tapin-Lingua, B. Benjelloun-Mlayah, and S. Rigolet, Synthetic-resin-free wood panel adhesives from low molecular mass lignin and tannin. *J. Adhesion Sci. Technol.* **24**, 1597–1610 (2010).
7. X. Li, A. Pizzi, X. Zhou, V. Fierro, and A. Celzard, Formaldehyde-free prorobitenidin/profisetinidin tannin/furanic foams based on alternative aldehydes: Glyoxal and glutaraldehyde. *J. Renew. Mater* **3**, 142–150 (2015).
8. F.J. Santiago-Medina, G. Foyer, A. Pizzi, S. Caillol, and L. Delmotte, Lignin-derived non-toxic aldehydes for ecofriendly tannin adhesives for wood panels. *Int. J. Adhes. Adhes.* **70**, 239–248 (2016).
9. U.H.B. Abdullah and A. Pizzi, Tannin-furfuryl alcohol wood panel adhesives without formaldehyde. *Eur. J. Wood Prod.* **71**, 131–132 (2013).
10. M.C. Basso, A. Pizzi, J. Polesel-Maris, L. Delmotte, B. Colin, and Y. Rogaume, MALDI-TOF and ¹³C NMR analysis of the cross-linking reaction of condensed tannins by triethyl phosphate. *Ind. Crops Prod.* (2016). DOI: 10.1016/j.indcrop.2016.11.031
11. F. Braghiroli, V. Fierro, M.T. Izquierdo, J. Parmentier, A. Pizzi, and A. Celzard, Nitrogen-doped carbon materials produced from hydrothermally treated tannin. *Carbon* **50**, 5411–5420 (2012).
12. F. Santiago-Medina, A. Pizzi, M.C. Basso, L. Delmotte, and A. Celzard, Polycondensation resins by flavonoid tannins reaction with amines. *Polymers* **9**(2), 37, 1–16 (2017).
13. R. Böhm, M. Hauptman, A. Pizzi, C. Friederich, and M.-P. Laborie, The chemical, kinetic and mechanical characterization of tannin-based adhesives with different crosslinking systems. *Int. J. Adhes. Adhes.* **68**, 1–8 (2016).
14. A. Sauget, X. Zhou, and A. Pizzi, MALDI-ToF analysis of tannin-resorcinol resins by alternative aldehydes. *J. Renew. Mater* **2**, 186–200 (2014).
15. A. Gandini, Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules* **41**(24), 9491–9504 (2008).
16. N. Essayem, R. Lopes de Sousa, and F. Rataboul, Procédé de préparation de 5-hydroxymethylfurfural, French patent application FR1154232 (2011).
17. X. Qi, M. Watanabe, and T.M. Aida, Sulfated zirconia as a solid acid catalyst for the dehydration of fructose to 5-hydroxymethylfurfural. *Catal. Commun.* **10**, 1771–1775 (2009).
18. C. Lansalot-Matras and C. Moreau, Dehydration of fructose into 5-hydroxymethylfurfural in the presence of ionic liquids. *Catal. Commun.* **2003**, 517–520 (2003).

19. D. Xien, J. Feng, and L. Genxiang, Dehydration of carbohydrates into 5-hydroxymethylfurfural in the presence of double micro-porous zeolite catalyst. *Chem. Intermediat.* **2**, 17–22 (2010).
20. J. Wang, C. Zhang, and P. OuYang, Advances in production and application of 5-hydroxymethylfurfural. *Chem. Ind. Eng. Prog.* **27**(5), 702–707 (2008).
21. S. De, S. Dutta, and B. Saha, Microwave assisted conversion of carbohydrates and biopolymers to 5-hydroxymethylfurfural with aluminium chloride catalyst in water. *Green Chem.* **13**, 2859–2868 (2011).
22. X. Qi, M. Watanabe, T.M. Aida, and R.L. Smith Jr., Catalytic conversion of fructose and glucose into 5-hydroxymethylfurfural in hot compressed water by microwave heating. *Catal. Commun.* **9**, 2244–2249 (2008).
23. T.S.S. Hansen, J.M. Woodley, and A. Riisager, Efficient microwave-assisted synthesis of 5-hydroxymethylfurfural from concentrated aqueous fructose. *Carbohydr. Res.* **344**, 2568–2572 (2009).
24. J.N. Chheda, Y. Roman-Leshkov, and J.A. Dumesic, Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and polysaccharides. *Green Chem.* **9**(4), 342–350 (2007).
25. F. Salak Asghari and H. Yoshida, Dehydration of fructose to 5-hydroxymethylfurfural in sub-critical water over heterogeneous zirconium phosphate catalysts. *Carbohydr. Res.* **341**, 2379–2387 (2006).
26. M. Bicker, D. Kaiser, L. Ott, and H. Vogel, Dehydration of D-fructose to hydroxymethylfurfural in sub- and supercritical fluids. *J. Supercrit. Fluid.* **36**, 118–126 (2005).
27. S.Q. Hu, Z.F. Zhang, J.L. Song, Y. Zhou, and B. Han, Efficient conversion of glucose into 5-hydroxymethylfurfural catalyzed by a common Lewis acid SnCl₄ in an ionic liquid. *Green Chem.* **11**(1), 1746–1749 (2009).
28. Y.J. Pagán-Torres, T. Wang, J.M.R. Gallo, B.H. Shanks, and J.A. Dumesic, Production of 5-hydroxymethylfurfural from glucose using a combination of Lewis and Brønsted acid catalysts in water in a biphasic reactor with an alkyl-phenol solvent. *ACS Catal.* **2**(6), 930–934 (2012).
29. A. Ranoux, K. Djanashvili, I.W.C.E. Arends, and U. Hanefeld, 5-Hydroxymethylfurfural synthesis from hexoses is autocatalytic. *ACS Catal.* **3**(4), 760–763 (2013).
30. A. Pizzi, R. Vosloo, F.A. Cameron, and E. Orovan, Self-neutralizing acid-set PF wood adhesives. *Holz Roh Werkst.* **44**, 229–234 (1986).
31. P. Navarrete, A. Pizzi, H. Pasch, K. Rode, and L. Delmotte, Characterisation of two maritime pine tannins as wood adhesives. *J. Adhes. Sci. Technol.* **27**, 2462–2479 (2013).
32. Y. Laigle, C. Kamoun, and A. Pizzi, Particleboard I.B. forecast by TMA bending in UF adhesives curing. *Holz Roh Werkst.* **56**, 154 (1998).
33. C. Zhao, S. Garnier, and A. Pizzi, Particleboard dry and wet IB forecasting by gel time and dry TMA bending in PF wood adhesives. *Holz Roh Werkst.* **56**, 402 (1998).
34. S. Garnier, Z. Huang, and A. Pizzi, Commercial tannin adhesives-bonded particleboard IB forecasting by TMA bending. *Holz Roh Werkst.* **59**, 46 (2001).
35. M. Lecourt, A. Pizzi, and P. Humphrey, Comparison of TMA and ABES as forecasting systems of wood bonding effectiveness. *Holz Roh Werkst.* **61**, 75–76 (2003).
36. European Norm EN 319, Perpendicular tensile strength of particleboards and fibreboards (1993).
37. FESYP Methods, Fédération Européenne des syndicats des fabricants de panneaux de particules, Brussels, Belgium (1979).
38. F. Pichelin, A. Pizzi, A. Früwald, and P. Triboulot, Exterior OSB preparation technology at high moisture content – Part 1: Transfer mechanisms and pressing parameters. *Holz Roh Werkst.* **59**, 256–265 (2001).
39. A. Pizzi, Wood and fiber panels technology, in *Lignocellulosic Fibers and Wood Handbook: Renewable Materials for Today's Environment*, M.N. Belgacem and A. Pizzi (Eds.), pp. 385–406, Wiley-Scrivener, New York (2016).
40. Z. Yuan, Y. Zhang, and C. Xu, Synthesis and thermo-mechanical properties of novolac phenol-hydroxymethyl furfural (PHMF) resin. *RSC Adv.* **4**, 31829–31835 (2014).
41. Y. Zhang, Production and applications of formaldehyde-free phenolic resins using 5-hydroxymethylfurfural derived from glucose in-situ, PhD thesis, The University of Western Ontario (2014). Electronic Thesis and Dissertation Repository, 2617. <http://ir.lib.uwo.ca/etd/2617>.
42. C. Xu, Y. Zhang, and Z. Yuan, Formaldehyde free phenolic resins, downstream products, their synthesis and use, US Patent application 20160355631, Application number 15/119030, Filing date 20/2/2015, assigned to The University of Western Ontario.