

## WOOD ADHESIVES FROM AGRICULTURAL BY-PRODUCTS: LIGNINS AND TANNINS FOR THE ELABORATION OF PARTICLEBOARDS

LAN PING,<sup>\*,\*\*</sup> FRANÇOIS GAMBIER,<sup>\*\*</sup> ANTONIO PIZZI,<sup>\*\*</sup> ZHOU DING GUO<sup>\*</sup> and  
NICOLAS BROSSE<sup>\*\*</sup>

<sup>\*</sup>*College of Wood Science and Technology, Nanjing Forestry University,  
Nanjing 210037, China*

<sup>\*\*</sup>*Lorraine University, Laboratory of Research and Study on Wood Materials LERMAB,  
Faculty of Sciences and Technologies, Bld des Aiguillettes, F-54500 Vandoeuvre-lès-Nancy, France*

Organosolv lignins were extracted from lignocellulosic raw materials (*Miscanthus x Giganteus* and Empty Fruit Palm Bunch) and condensed tannins were extracted from grape by-product in an aqueous medium using different catalysts. Resin formulations with total polyphenolic contents (tannin and/or lignin) ranging from 70% to 95% of the total resin solids content were employed for the elaboration of particleboards. Mixtures of glyoxylated lignin/tannin and pure tannin were produced and tested. The importance of the nature of the basic reagent used for the extraction of tannins from grape pomace was demonstrated. Most of the adhesives produced yielded good internal bond strength results of the panels, enough to meet relevant international standard specifications for interior-grade panels (European Norm EN 312).

**Keywords:** Lignin, tannin, grape pomace, adhesives

### INTRODUCTION

Wood adhesives from renewable raw materials have been a topic of considerable interest for many years and constitute an area of active research. Large quantities of lignin are expected to be produced in future biorefineries as a by-product of biofuel production. In fact, the effective utilization of lignocellulosic feedstock necessitates the development of pretreatment technologies that are necessary to separate the three biopolymers (i.e. cellulose, hemicellulose and lignin).<sup>1</sup> Among all the pretreatment methods currently studied for the production of biofuel, the ethanol organosolv process seems to be very promising. As reported, it has been recently optimized for different raw materials, such as poplar,<sup>2</sup> pine,<sup>3</sup> miscanthus<sup>4,5</sup> and palm biomass.<sup>6</sup> This procedure has the ability to cause an extensive removal of hemicelluloses under mild conditions, with no significant cellulose degradation and to generate a large amount of high-quality lignin with valuable properties. The literature on the use of lignins to prepare wood adhesives is very extensive.<sup>7</sup> Recently, we described lignosulfonate lignin-based wood

adhesives satisfying the requirements of relevant international standards for the manufacture of wood particleboard.<sup>8</sup> These lignin-based wood adhesives did not use any formaldehyde in their formulation, but rather glyoxal, a non-volatile, non-toxic aldehyde. The adhesives yielded good internal bond strength results for the panels and passed relevant international standard specifications for exterior-grade panels.

Tannins have already been used commercially for 30 years.<sup>9-13</sup> Condensed tannins are generally extracted from the bark of various trees.<sup>14-16</sup> Grape is one of the world's largest fruit crops and this production generates a substantial volume of solid organic by-product. Only small amounts of these by-products are up-graded or recycled; the pomace is used for animal feed or compost, without any pre-treatment. The remaining solid residues retain high levels of condensed tannins because of low extraction during winemaking. A few preliminary experiments concerning tannin extraction from grape pomace have been recently reported in previous communications.<sup>17,18</sup>

The ability of green adhesives to make a significant impact as a substitute for polymeric materials depends on the availability of low-price biopolymer fractions (lignins and tannins) in large quantities and of high-quality polyphenolic extracts, displaying good chemical reactivity towards crosslinking agents (e.g. formaldehyde, glyoxal etc.). In the present study, we described economically and environmentally valuable extractions and utilizations of polyphenolic fractions for the elaboration of green adhesive formulations. Organosolv lignin and condensed tannins were extracted from miscanthus straw, palm oil residues and grape pomace. Then, we prepared the first particleboards based on grape pomace extract and miscanthus lignin for interior-grade panels.

## EXPERIMENTAL

### Material

The raw *Miscanthus x giganteus* was harvested in spring 2008 from Courcelle-Chaussy (France). The air-dried miscanthus was milled to a particle size of 1-3 mm using a Wiley mill. The untreated feedstock contained 25% Klason lignin, 37% cellulose and 36% hemicellulose. EPFB was collected from oil palm cultivation in the Tali Air Estate (Sime Darby), Bagan Serai, Perak, Malaysia. It was washed rigorously with water and dried in the sun before it was sent by air mail to France. Total polyphenol content of EFB was gravimetrically determined as Klason lignin (32.2%) and as soluble lignins (2.6%) by UV quantification. The raw material also contained 42.6% glucans and 1.2% ash. The pomace samples corresponded to mixtures of by-products of the winemaking process of red grape variety (*Vitis vinifera*), growing in the south-east of France and were provided by a French distillery. The air-dried grape pomace was composed by grape skin, seeds and stalks manually separated. It was stored at room temperature during the course of this study. All chemical reagents used in this study were purchased from VWR International and used as received.

### Pretreatment: Organosolv lignin extraction

A 1.0-L glass-lined pressure Parr reactor with a Parr 4842 temperature controller (Parr Instrument Company, Moline, IL) was employed for the pretreatment. Twenty grams of biomass (EPFB or miscanthus, dry mass) was treated with an ethanol/water mixture in a volume ratio of 65:35 with sulphuric acid as a catalyst. The solid-to-liquid ratio used was 1:8. The mixture was stirred continuously and heated at a rate of ~3 °C/min. Depending on the experiment conditions, the pressure increased to 15-20 bars. After the desired residence time was reached, the pretreated biomass was washed three times with 150

mL of 60 °C ethanol-water in an 8:2 ratio and air-dried overnight. Ethanol Organosolv Lignin (EOL) was precipitated out by adding three volumes of water to the combined washes.

### Glyoxylation of lignin

The EOL powder (29.5 parts by mass) was gradually added until 38.4 parts water while sodium hydroxide solution (30%) was added periodically to maintain the pH of the solution between 12 and 12.5 for better dissolution of the lignin powder, which was also facilitated by vigorous stirring. A 250-mL flat-bottom flask equipped with a condenser, thermometer and magnetic stir bar was charged with the above solution and heated to 58 °C. After the lignin was totally dissolved, 17.5 parts by mass glyoxal (40% in water) was added and the lignin solution was maintained at pH 12-12.5, with a magnetic stirrer on a hot plate for 8 hours. The total solids contents were of about 37%. The glyoxal is a non-toxic aldehyde, non-volatile, but less reactive than formaldehyde.

### Tannin extraction

Twenty grams (oven-dry matter) of grape pomace were treated with an aqueous solution of NaOH, Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> (2.5% w/w, see Table 1) in the presence of Na<sub>2</sub>SO<sub>3</sub> (2.5% w/w) with a solid-to-liquid ratio of 1:8. The reaction mixture was heated at different extraction parameters reported in Table 1. The treatments were carried out in a round bottle flask connected to a water condenser. After heating, the pomace was cooled, washed and filtered through filter paper. The washed liquid was evaporated to a moderate concentration (rotary evaporator, temperature: 60 °C), then lyophilised to yield lyophilised tannins. Per one sample of each solid residue and lyophilised tannins was separated and stored in a freezer at -5 °C before analysis.

### Tannin analysis

FTIR spectrum was obtained on a Nexus 870 FTIR spectrometer, tannins (0.2 mg) were added into KBr powder (30 mg), mixed and ground to powder, with a diameter of 2 µm, then pressed to a small piece to test.

The gelation time (T-gel) of tannin was referred to as the working time of tannin towards formaldehyde from a colloidal solution to become a solid or semi-solid jelly or gel. About 10 g of a 30% (w/w) of lyophilised tannin solution, 5% of powdered *para*-formaldehyde on a tannin dry and solid matter basis were added to a test tube and placed in a water bath, which was maintained at boiling temperature (just below 100 °C) at normal atmospheric pressure. The time taken to reach the gel point was recorded during constant stirring with the aid of a wire spring and a stopwatch. The test was duplicated and the average value was reported.

### TMA experiments

Modulus of elasticity (MOE) of the tannin formulations were studied using a thermal mechanical analyzer. The experiments were conducted under the same conditions: heat rate = 10 °C/min, 30 mg of resin, in the temperature range 25-250 °C. The thermomechanical analyzer used was a Mettler Toledo TMA40. The software used for data treatment was STARE. Deflection curves that allow MOE determination have been obtained by the three-point bending TMA mode. The maximum MOE value and its increase as a function of time or temperature for wood-resin systems is a good indication of the possible end performance of the adhesive system tested. The composition of different glue mixes for this test was 50/50 and 40/60 lignin/tannin proportion on the solids content basis (respectively formulation F1 and F2, Table 2).

### Resin adhesive preparation

A tannin solution in water was prepared with 45% concentration and its pH was adjusted to 10 with 33% NaOH water solution. It was added 6% (based on tannin) of hexamine at 33% solution in water as a hardener. Then the glyoxylated lignin was mixed with this tannin solution.

### Particleboard manufacture and testing

One-layer laboratory particleboards with the dimension of 350 × 300 × 16 mm<sup>3</sup> were prepared using only core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) wood particles at 35.7 kg/cm<sup>2</sup> (3.5 × 10<sup>6</sup> Pa) maximum pressure and 190-195 °C press temperature. 10% (w/w based on dry particles) of adhesive resin solid was loaded. The total pressing time was 7.5 minutes. The particleboards were tested for dry internal bond (IB), a tensile strength test that is a relevant international standard test (European Norm EN 312, wood particleboard specifications, 1995).

## RESULTS AND DISCUSSION

### Extraction of polyphenolics

The ethanol organosolv lignin was extracted from lignocellulosic starting materials (miscanthus and empty palm fruit bunch) according a previously described procedure<sup>5,6</sup> and the results are given in Figure 1 and Table 1. This procedure allowed a fractionation of the three main constituents of raw materials with high recovery yields. 11 to 13% and 14 to 17% (w/w based on raw material) of lignin were isolated respectively from miscanthus and oil palm biomass after precipitation of organosolv lignin by addition of water in the ethanol-water solution. Because of its low chemical reactivity, it is not possible to use lignin without an activation step before the introduction to the phenol-formaldehyde synthesis. Thus, the glyoxalation of organosolv lignin was performed in a basic medium by the addition of glyoxal.

The tannins were extracted from grape pomace in basic medium at 100 °C, according to a previously described procedure (Fig. 1).<sup>17,18</sup> The conditions given in Table 1 comprise an aqueous solution of NaOH, Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub> in the presence of Na<sub>2</sub>SO<sub>3</sub>. At the end of the treatment, a lyophilisation of the liquid phase yielded a crude residue.

### Characterization of extracts

FT-IR was used to determine the functional groups and the molecular structures of grape pomace tannins (Fig. 2). The band at 3218 cm<sup>-1</sup> was assigned to OH stretching vibration. The bands at 1619 cm<sup>-1</sup> and 1411 cm<sup>-1</sup> are due to aromatic frame stretching vibration. A very weak band around 1745 cm<sup>-1</sup> was assigned to carbonyl stretching, which could be attributed to the catechic acid rearrangement occurring during the extraction process.<sup>19</sup>

Table 1  
Experimental conditions and extract yields

Polyphenol	Raw material	Experimental conditions	Yield, % <sup>a</sup>
Organosolv lignin	Miscanthus	170 °C, 60 min, 0.9% H <sub>2</sub> SO <sub>4</sub>	11
		180 °C, 60 min, 0.9% H <sub>2</sub> SO <sub>4</sub>	8
	EPFB	170 °C, 60 min, 0.9% H <sub>2</sub> SO <sub>4</sub>	14
		190 °C, 60 min, 0.9% H <sub>2</sub> SO <sub>4</sub>	8
		Conditions 1 <sup>b</sup> : NaOH, 2.5%, Na <sub>2</sub> SO <sub>3</sub> , 2.5%	27
Tannins	Grape pomace	Conditions 2 <sup>b</sup> : NaHCO <sub>3</sub> , 2.5%, Na <sub>2</sub> SO <sub>3</sub> , 2.5%	20
		Conditions 3 <sup>b</sup> : Na <sub>2</sub> CO <sub>3</sub> , 2.5%, Na <sub>2</sub> SO <sub>3</sub> , 2.5%	22

<sup>a</sup> Yield of pure polyphenols, calculated from the raw material (oven dry mass)

<sup>b</sup> 120 min, 100 °C in water

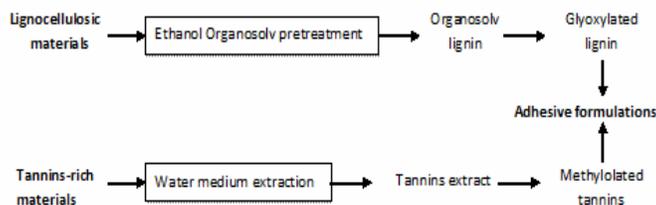


Figure 1: Schematic of tannin extraction

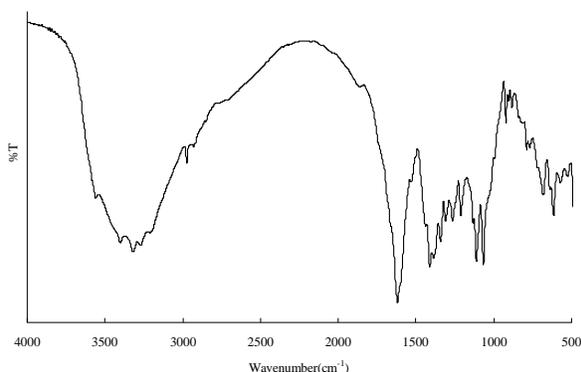


Figure 2: FT-IR spectrum of grape pomace tannins

This observation is in accordance with previously described  $^{13}\text{C}$  NMR results.<sup>17,18</sup>

The formation of this rearrangement product should affect the more reactive A aromatic ring of the catechin moiety and consequently should decrease the reactivity toward formaldehyde. In our case, a very low catechinic acid content is attested by FT-IR, suggesting a high reactivity of the extracts towards crosslinking reactions.

Gel times of the tannin fractions isolated under conditions 1, 2 and 3 (see Table 1), were 95 seconds (pH 5.9), 206 seconds (pH 5.9) and 108 seconds (pH 6.3), respectively. Gel time is an indication of the reactivity of the sites of tannin molecules towards formaldehyde. Thus, the tannins obtained in this study can be classified under the same group as the faster reacting tannins previously described, such as pine bark and pecan nut pith extracts.<sup>20</sup>

### TMA experiments and particleboards

Mixtures of glyoxylated lignin/tannin (50/50, F1, and 40/60, F2) and of grape pomace tannin/formaldehyde (F3, F4 and F5) were prepared and the rigidity of the bonded wood joints was studied by TMA as a function of

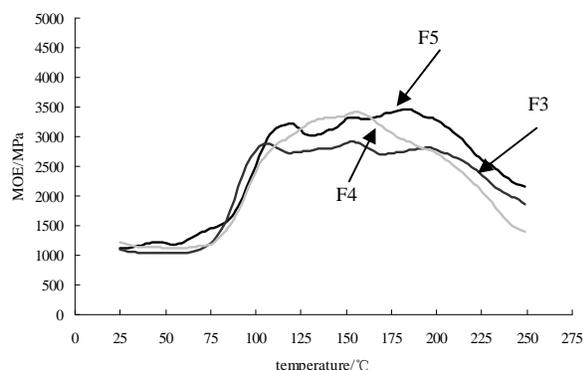


Figure 3: TMA measuring MOE as a function of temperature to describe the curing of grape pomace resins F3, F4 and F5

temperature. MOE at 195 °C, corresponding to the press temperature of our laboratory equipment, is given in Table 2.

The curves of the modulus of elasticity (MOE) as a function of increasing temperature for the resins are also given in Figure 3 for formulations F3, F4 and F5. The TMA results of the curing of the mixture lignin/tannin 50/50 (fraction F1, see Table 2) indicate relatively low wood-joint strength. On the basis of the known reactivity of tannins toward crosslinking reactions, we considered the addition of a further amount of tannins into the mixture. Thus, the mixture lignin/tannin 40/60 (formulation F2) gave a higher value of MOE (2621 MPa). Concerning the grape pomace tannin extracts, it is interesting to observe different TMA behaviors as a function of the nature of the catalyst used during the extraction. From Figure 3, it appears that the MOE of F3 and F5 keep a stable value in the range of temperatures corresponding to wood panel press conditions (190 °C < T < 250 °C), whereas for F4 we observe a decrease in this range of temperatures. Table 2 clearly shows that at 195 °C, F5 gives the best performance with a MOE of ~3323 MPa.

Table 2  
Adhesive formulation compositions, thermomechanical analysis and particleboard testing

Formulation number	Composition <sup>a</sup>	TMA		Particleboard	
		MOE <sup>b</sup> at 195 °C (MPa)	Density (kg/m <sup>3</sup> )	IB <sup>c</sup> (MPa)	
F1	Glyoxylated lignin + tannins 50/50	2171	695	0.33 ± 0.02	
F2	Glyoxylated lignin + tannins 40/60	2621	696	0.41 ± 0.05	
F3	Grape tannins <sup>d</sup> Conditions 1	2812	696.3	0.23 ± 0.01	
F4	Grape tannins <sup>e</sup> Conditions 2	2777	692.6	0.26 ± 0.02	
F5	Grape tannins <sup>f</sup> Conditions 3	3323	706.1	0.45 ± 0.06	

<sup>a</sup> solutions in water; <sup>b</sup> Modulus of elasticity; <sup>c</sup> Internal bond strength;

<sup>d</sup> extracted by NaOH (2.5%) + Na<sub>2</sub>SO<sub>3</sub> (2.5%); 40% based on weight of dry pomace;

<sup>e</sup> extracted by NaHCO<sub>3</sub> (2.5%) + Na<sub>2</sub>SO<sub>3</sub> (2.5%); 45% based on weight of dry pomace;

<sup>f</sup> extracted by Na<sub>2</sub>CO<sub>3</sub> (2.5%) + Na<sub>2</sub>SO<sub>3</sub> (2.5%); 30% based on weight of dry pomace

### Particleboards

The adhesive formulations were then tested for application to wood panels, such as particleboards. The internal bond (IB) strengths of the panels given in Table 2 are direct measures of the performance of the adhesives.

It can be seen that the formulation F1 does not satisfy the relevant standard specifications for interior-grade type wood particleboard (IB > 0.35 MPa), being slightly lower. It appears that the addition of a further amount of tannins in the glue mix allows obtaining formulation F2, which is according to the standard.

Concerning the grape pomace based formulations (F3-F5), the IB values given in Table 2 confirm the importance of the nature of the reagent used for the extraction of tannins. The utilization of sodium hydroxide or sodium hydrogenocarbonate (respectively, F3 and F4) gave a low IB value, which does not satisfy the IB strength requirements. On the other hand, the formulation F5 obtained through the utilization of sodium carbonate gave a very good result. The IB strength value (0.45 MPa) of the panel satisfied the requirements of international standard specifications. Interestingly, formulation F5 also appeared to yield higher density material (~710 kg/m<sup>3</sup>). This observation can be explained by an extensive immobilization of the network involving the reactive tannin molecules, causing a higher density of crosslinking and also higher strength.

### CONCLUSIONS

In this study, we examined the extraction of tannins and lignins, respectively, from grape pomace in a water medium and from lignocellulosic feedstocks using an ethanol organosolv process. The polyphenolic extracts were characterized and used for the elaboration of resin formulations in which the total polyphenolic contents (tannin and/or lignin) ranged from 70% to 95%. The resins were tested and employed for the elaboration of particleboards. The adhesives yielded good internal bond strength results of the panels, satisfying relevant international standard specifications for interior-grade panels.

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