Organosolv Wheat Straw Lignin as a Phenol Substitute for Green Phenolic Resins

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Organosolv wheat straw lignin extracted using the CIMV process[TM] is a linear, low molecular weight, and natural phenolic oligomer. In this study, organosolv wheat straw lignin was tested as a substitute for 50% to 70% of the phenol in a phenol-formaldehyde-resol resin. The lignin was used without any chemical modification in a one-step synthesis reaction. Parameters such as reaction time and formaldehyde-to-phenol sources (phenol + lignin) mass ratios were optimized to achieve the requirements for industrial wood adhesives in terms of pH, viscosity, and dry matter. For the first time, the formaldehyde ratio was studied in order to reduce resin residual free formaldehyde below 1%. Lignin-phenol-formaldehyde resins were successfully synthesized up to a phenol substitution rate of 70% and showed physico-chemical properties close to standard phenol-formaldehyde resins. The thermo-mechanical properties analyzed in dynamic load thermo mechanical analysis were similar to those of the reference resins. Plywood panels manufactured using these lignin-based resins reached the specifications for industrial panels according to the French standard for exterior plywood panels. Moreover, the formaldehyde content of these plywoods was low enough to satisfy even the most rigorous legislation.

INTRODUCTION

Phenolic resins are widely used as thermosetting polymers. Resoles are base-catalysed resins in which formaldehyde is in excess. Because of their good mechanical properties, durability, and high water resistance (Gardziella *et al.* 1985; Pilato 2010) they are used in wood manufacturing and in particular, in exterior grade wood-based composites (Ibeh 1999). As ecological factors are being taken into consideration more often, phenol, because of its toxicity and its carcinogenic effect, is being replaced by green-products such as lignins in bio-based resins.

In view of lignin monomers, an electrophilic addition between formaldehyde and free *ortho* positions of guaiacyl and *p*-hydroxyphenyl units may occur. Despite the chemical similarities of lignin to phenol, the synthesis of formo-phenolic resin (PF) using unmodified lignin in place of phenol has provided very few satisfactory results (Hu *et al.* 2011). Consequently, many studies have focused on lignin phenolation, methylolation, and co-condensation with phenol to enhance its reactivity (Alonso *et al.* 2005; El Mansouri *et al.* 2007; Wang *et al.* 2009).

Methylolation of ammonium lignosulfonates allows a substitution of phenol up to 35% (w/w) in resoles (Alonso *et al.* 2001, 2004b). The physico-chemical and curing characteristics of these resoles are close to those of PF resins (Alonso *et al.* 2004a, 2006). They also comply with the requirements for plywood adhesives (Alonso *et al.* 2004b). Unmodified kraft lignin can only substitute 30% of phenol for plywood adhesives applications (Kouisni *et al*. 2011), whereas a pre-phenolation of kraft lignin increased the phenol substitution content up to 40% (Abdelwahab and Nassar 2011). Pre-phenolated alkali lignins from different feedstocks have substituted up to 50% of phenol to produce resoles for adhesive applications (Khan and Ashraf 2007). Adhesive strength and shear properties of the panels are close to those obtained with PF resins. However, the source of lignin clearly impacts the final resin properties. As hardwood lignin provides more syringyl units, it is less reactive and a less efficient substitute for phenol in the synthesis of resol resins than softwood lignin (Wang *et al.* 2009). Bagasse lignin is the best candidate for substitution of phenol in resoles (Khan and Ashraf 2007).

The low reactivity of lignosulfonates and kraft and alkali lignins is partially overcome by pre-phenolation and pre-methylolation of lignin. Organosolv processes use less severe conditions than other extraction processes, resulting in organosolv lignins that are less condensed and more reactive than other lignins.

In the initial studies, unmodified eucalyptus acetosolv lignin was considered as a filler, and no more than 20% could substitute phenol without decreasing the plywood mechanical strength (Vazquez *et al.* 1995). The methylolation of eucalyptus acetosolv lignin allowed a phenol substitution up to 40% (Vazquez *et al.* 1997). The LPF plywood panels were similar to those obtained with commercial resins, with respect to the knife and strength-adhesion tests. Wang *et al.* (2009) substituted up to 75% of phenol with unmodified pine organosolv lignin in a one-step co-condensation reaction without determining free residual formaldehyde. At over 50% substitution, the process of curing was deferred.

Most studies show that it is possible to substitute a small part of phenol with lignin in phenolic resins, but generally only after lignin modification, which prohibits any large-scale development. Previously, there has been no optimisation of the LPF synthesis to generate a product that satisfies all industrial requirements and can be developed industrially.

In this study, an organosolv lignin was used as a phenol source to synthesise bio-based phenolic resins. The selected lignin was extracted from wheat straw using a mixture of acetic and formic acids, according to the organosolv pretreatment developed by CIMV (Paris, France) (Delmas and Avignon 2000; Delmas 2008; Delmas *et al.* 2009). Its high purity, low molecular weight, high hydroxyl groups content, and especially its linear fragments make this lignin unique and particularly interesting for this application (Banoub and Delmas 2003; Banoub *et al.* 2007, 2015). In addition to its qualities, this particular lignin, named Biolignin[TM], is valuable since CIMV is building its first pre-industrial demonstration plant as part of the European project 2G-BIOPIC (Horizon 2020, Grant Agreement n°657867). Previous studies have underlined the feasibility of replacing phenol with this lignin in resoles (Delmas and Benjelloun-Mlayah 2013; O'Donohue 2014; Hubbard *et al.* 2015).

This work presents for the first time a lignin-based resin that satisfies all industrial requirements for a wood adhesive resin including a residual free formaldehyde content under 1%. The synthesis of this lignin-phenol-formaldehyde resin is a one-step reaction where at least 50% of the phenol is replaced by Biolignin[TM] without any prior modification.

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The resulting lignin-based resins were used to manufacture plywood panels according to industrial specifications.

In the following text, the abbreviations below are used: BL for the lignin that was used (Biolignin^{TM}), PF for the unsubstituted phenol-formaldehyde resole, BPF for the substituted BL-phenol-formaldehyde resole, and F/(P+BL) for the formaldehyde-to-phenol sources mass ratio.

EXPERIMENTAL

The following chemicals were purchased from Panreac (Castellar del Vallès, Spain): phenol crystalline (USP, BP, Ph. Eur.) pharma grade (>99%), formaldehyde solution (about 37% in water, precisely titrated), and sodium hydroxide pellets were used in the synthesis of phenolic resins. Tetrahydrofuran (THF), methanol, and 1,4-dioxane were of HPLC grade. Pyridine (99%) and hydroxylamine hydrochloride were reagent grade (99%). N-hydroxy-1,8-naphtalimide (97%), chromium (III) acetylacetanoate (99.99%), and 2-chloro-1,3,2-dioxaphospholane (97%) were purchased from Sigma-Aldrich (Saint-Quentin-Fallavier, France).

Biolignin^{TM} (BL) was extracted at a pilot scale from wheat straw using a mixture of acetic acid/formic acid/water (55:30:15, w/w/w) (Delmas and Avignon 2000; Delmas 2008; Delmas *et al.* 2009). After 3.5 h at 105 ± 2 °C, extraction liquors containing lignin and pentoses were concentrated until 60% dry matter remained. BL was separated from the pentoses following the dispersion of lignin particles in water and filtration on a press filter (Delmas and Benjelloun-Mlayah 2011b). The BL dry matter was 60 to 65% of the final product.

Characterization of BL
Gel permeation chromatography (GPC)

The molecular-average weight of the BL samples was determined using gel permeation chromatography (GPC). GPC analyses were carried out on a Waters 1515 isocratic HPLC pump (Saint-Quentin-en-Yvelines, France) equipped with a Waters 2414 refractive index detector. Three GPC PL-gel columns (300×7.5 mm, 5-µm, styrene-divinyl-benzene; Agilent, Santa Clara, CA, USA) were connected in a series (100 Å, 500 Å, and 1000 Å), with the following operating conditions: eluent, THF; temperature, 30 °C; sample concentration, 10 mg/mL in methanol/1,4-dioxane/THF (1:1:6, v/v/v); injection volume, 20 µL; and flow rate, 1.2 mL/min.

The polystyrene (PS) standards used for the GPC analyses had molecular weights of 7000, 4910, 4100, 3180, 2590, 2170, 1530, 990, and 770 Da. The standard concentration of THF was set at 2 mg/mL. The molecular weight of lignin was measured relative to polystyrene standards and was therefore not absolute.

Klason lignin content

Acid insoluble lignin (AIL) was determined by an adapted TAPPI standard 222 om-11 (2011) and adjusted for BL. Acid soluble lignin (ASL) was determined according to TAPPI standard UM250 (1985). The Klason lignin content was the sum of AIL and ASL.

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Residual hemicelluloses content

The residual hemicelluloses content was determined by an adapted TAPPI standard method 223 CM-01 (2001) and adjusted for BL. Quantification included HPLC titration of furfural produced by the acid hydrolysis of hemicelluloses and dehydration of xylose.

Protein content

Nitrogen was quantified using elementary analysis. The value 5.4 was used as the correcting factor to determine the protein content for wheat straw (protein content = N × 5.4) (Mariotti *et al.* 2008).

Quantitative ^{31}P NMR: alkyl and aryl hydroxyl groups content

Approximately 30 mg of dried lignin was transferred into a 1.5-mL sample vial, and 400 µL of a freshly distilled pyridine/deuterated chloroform mixture (1.6:1, v/v) was added. The sample vial was flushed with argon gas, sealed, and magnetically stirred at room temperature until complete dissolution.

Using the pyridine/deuterated chloroform mixture as solvent, N-hydroxy-1,8-naphtalimide (0.01mmol/ml) and chromium (III) acetylacetonate (0.0143mmol/ml) were used as internal standard and relaxation agent, respectively. To the sample vial, 100 µL of the internal standard and 100µL of the relaxation agent were added. Finally, 100 µL of the derivatization agent, 2-chloro-1,3,2-dioxaphospholane (Fig. 1), was added, and the mixture was left at room temperature for 20 min under continuous stirring. The prepared sample solution was transferred into a 5-mm NMR tube and immediately analysed.
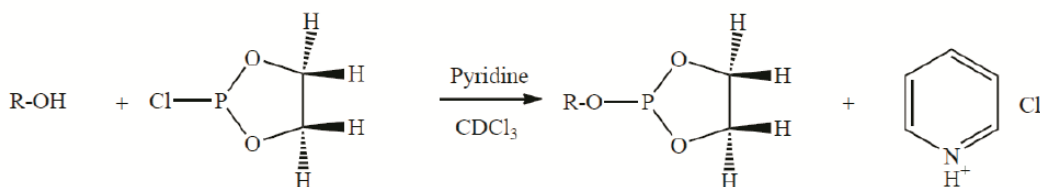
Fig. 1. Derivatization of hydroxyl groups

The spectra were acquired using a Bruker Avance 400 MHz spectrometer (Karlsruhe, Germany) equipped with a 5-mm TBO BB-1H/31P/D Z-GRD Z104586/0001 probe. A sweep width of 10000 Hz was observed, and spectra were accumulated with a time delay of 25 s between pulses. A pulse width causing a 90° flip angle was used. A 4 Hz line broadening was used while processing the spectra, and 128 scans were collected. All chemical shifts were relative to the reaction product of water with the phosphitylating reagent, which produces a sharp signal in pyridine/CDCl$_3$ at 121.1 ppm (Argyropoulos 1994).

Characterization of Phenol Formaldehyde Resin

Viscosity

Resin viscosity was determined at 20 °C using a Brookfield viscometer ViscoBasicPlus (Fungilab, Barcelona, Spain).

Dry matter of PF resin

According to standard method NF-EN-827 (2006), the resin dry matter was determined after drying at 105 °C during 3 h.

Formaldehyde quantification in the resin

The residual formaldehyde was determined in accordance with NF EN 11402 (2005). A blank titration containing lignin was necessary to limit any interference.

Quantitative ^{31}P-NMR: alkyl and aryl hydroxyl groups content

Unsubstituted and substituted phenolic resins were analysed using ^{31}P-NMR. The resins were precipitated at pH 2 by adding a 12%-hydrochloric acid solution. The solid was washed with distilled water until the liquid reached pH 7. The solid was then frozen to minus 20 °C before lyophilisation. The dry solid was derivatized with 2-chloro-1,3,2-dioxaphospholane, following the same treatment as described above for lignin, and then analysed using ^{31}P-NMR following the same protocol.

Dynamic load thermo-mechanical analysis (DLTMA)

Because wood has a significant impact on PF curing kinetics and on the PF strength development (Laborie 2002), PF resins curing in a wood joint were examined. The hardening of the resin can be evaluated using DLTMA (Lu and Pizzi 1998; Garcia and Pizzi 1998; Onic *et al.* 1998). Wood beech plies of 0.6-mm thickness were cut into 14×5 mm samples. Between 23 and 24 mg of resin was spread between two plies. The resulting panel was then tested with a Mettler 840 DLTMA apparatus (Viroflay, France) at three bending points. The experiments were conducted at a heating rate of 10 °C/min from 30 °C to 250 °C under a crenel variation of strength of 0.1 to 0.5 N (6 s/6 s). The thickness evolution was registered according to time and temperature. The data was automatically converted using STARe software (Mettler-Toledo, Viroflay, France) according to the Young modulus (*E*), due to the relation between deflection and force. The maximal *E* value gave a good indication on the final mechanical properties and performance of the adhesive.

Phenol Formaldehyde Resin Synthesis

Synthesis of phenol formaldehyde resins

Because of the exothermicity of the reaction between phenol-formaldehyde and sodium hydroxide, the reaction mixture was heated by the addition of sodium hydroxide. However, as previously mentioned by El Mansouri *et al.* (2007), the addition of the whole sodium hydroxide at the initial stage resulted in a dramatic increase of the mixture temperature. As a consequence, the reaction was not controllable. The solution proposed by these authors was to sequence the addition of sodium hydroxide, which prevented the runaway reaction.

In a 250-mL glass reactor, 40.4g of phenol, 17.3 g of water, and 69.2 g of formaldehyde were combined and heated between 50 and 55 °C under mechanical stirring. Next, 25% to 50% of the total amount of a 50% (w/w) sodium hydroxide solution (17.6 g) was added under stirring. The remaining sodium hydroxide was regularly added to reach and maintain a temperature over 90 °C and preferably, over 100 °C. The reaction time (temperature over 90 °C) was set in order to reach the required viscosity that ranged from 300 cP to 800 cP at 20 °C. This reaction time was around 60 min for the unsubstituted phenolic resin. The resin was analysed at room temperature and then stored at 4 °C.

For BPF synthesis, up to 50% phenol substitution, phenol, formaldehyde and water were combined and heated between 50 and 55 °C under mechanical stirring. Then, BL was slowly added under stirring to the mixture just before the first addition of 25% of the total amount of a sodium hydroxide solution (50% (w/w)). Next, 25% to 50% of the total amount of the sodium hydroxide solution (50% (w/w)) (17.6 g) was added under stirring. The

remaining sodium hydroxide was regularly added to reach and maintain a temperature over 90 °C and preferably, over 100 °C. The reaction time (temperature over 90 °C) was set in order to reach the required viscosity that ranged from 300 cP to 800 cP at 20 °C. For substitution rates of phenol higher than 50%, the protocol is the same as the previous one except that the addition of BL was divided into two equal parts, the first of which was added at 50 °C and the second one was added when the mix temperature reached 80 °C.

For each substitution rate, the reaction time was adapted for the resin to reach the required viscosity (300 cP to 800 cP at 20 °C).

Plywood Panel
Plywood manufacture

Wood beech veneer (20 cm × 20 cm × 1 mm) was dried and kept away from moisture until use. Each side of two dry veneer plies was coated with 8 g of adhesives (PF mixed with 30% of $CaCO_3$). These two plies were assembled immediately with three unglued plies in such a way that every glued side was in contact with an unglued ply. During assembly, the grain of the glued plies had to be perpendicular to the grain of the unglued ones. The sample consisting of 5 plies was conditioned for at least 15 min at room temperature under a 15-kg weight. The assembled wood specimens were hot-pressed at 7 N/mm² and 145 °C for 6 min.

Plywood characterization

The variables considered in the evaluation of the quality of the glue-bond were shear strength and cohesive wood failure (Dieste *et al.* 2009). The shear strength was measured according to standard NF EN 314-1 (2005). Cohesive failure was evaluated by visual inspection. A total of 5 specimens were studied per plywood. The shear strength and adhesion values were used to classify the panel according to the certification NF exterior CTB X standard (AFNOR certification of plywood panels for exterior utilisation, in accordance with NF EN 636-3 (2012) and NF EN 314-2 (1993) with a bonding class 3).

Formaldehyde content

The formaldehyde content within the plywood panels was measured according to the standard method NF EN 120 (1993) and the perforator method, the most common method used in European industries (Park *et al.* 2011). Formaldehyde was extracted from samples of plywood panels by boiling in toluene for 2 h. The formaldehyde concentration was determined using acetylacetone analysis procedures. The perforator value was expressed as milligrams of free formaldehyde per 100 g of dry board.

RESULTS AND DISCUSSION

Characterization of Lignin

The structure of wheat straw BL has been widely studied (Banoub and Delmas 2003; Banoub *et al.* 2007, 2015; Delmas *et al.* 2011a). A model of the structure is proposed in Fig. 2. The molecular weight, dry matter, ash content, Klason lignin content, and residual hemicelluloses content of BL were determined (Table 1). BL was considered as a phenolic oligomer of less than 10 units. It had a lower molecular weight than kraft lignin (> 10 kDa) or lignosulfonate (> 60 kDa). Its purity was also higher than conventional lignins due to the biorefining process conditions (Delmas and Avignon 2000; Delmas *et al.* 2009).

The BL sample was analysed by ^{31}P-NMR to quantify its hydroxyl groups (Table 2). ^{31}P-NMR analysis showed that BL extracted from wheat straw had free phenolic hydroxyl groups. The presence of guaiacyl and *p*-hydroxyphenyl units is very interesting because they can react with aldehydes under basic conditions.
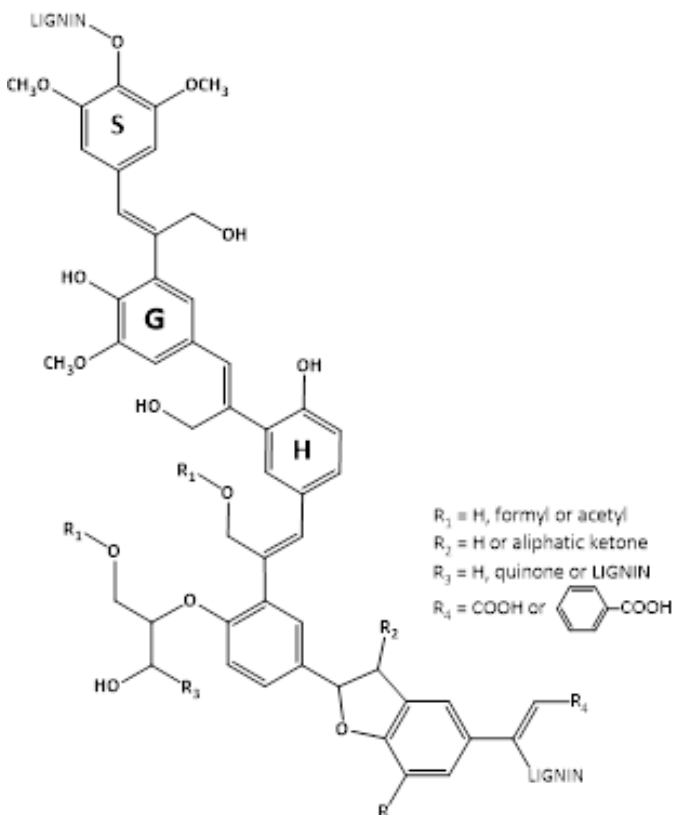

Fig. 2. BL proposed structure (Banoub *et al.* 2007, Crestini *et al.* 2011)

Table 1. Composition and Characterization of BL

Molecular Weight (Mn)	900 Da
Molecular Weight (Mw)	1900 Da
Polydispersity	2.1
Dry matter (DM)	64%
Ash content (%/DM)	0.60%
Klason content (%/DM)	88.5%
Residual hemicelluloses content (%/DM)	3.1%
Protein content (%/DM)	7.8%

Table 2. ^{31}P-NMR Quantification of Hydroxyl Groups of BL (mmol/g)

|	S and condensed G	Noncondensed G	Noncondensed H	-COOH	Aliphatic	Active sites
BL	0.70	0.86	0.18	0.27	1.11	1.22
Peak (ppm)	132.1 to 131.4	130.6 to 129.6	128.6 to 128	128 to 126.8	133.6 to 132.1	

Preliminary Tests

In this study, the chosen application for the phenolic resin was as a plywood adhesive. The industrial reference (PFref) was a phenolic resin for plywood adhesives supplied by ROLKEM-NANKAI Plywood (Mourenx, France). The industrial requirements for this kind of resin are listed in Table 3.

Table 3. Requirements for Phenolic Resins used as Plywood Adhesives

Dry Matter	> 44%
pH	11 to 12
Viscosity at 20°C	300 to 800 cP
Residual Free Formaldehyde Content	< 1% (Pilato 2010)

The standard protocol for synthesising commercial phenolic resin was used to produce a resin containing 50% BL as its phenol source. Neither process optimisation nor formulation has been studied previously, except for the reduction of reaction times for the substituted resin to reach an acceptable viscosity. The resulting resin was analysed by ^{31}P-NMR to identify the possible modification of reactive sites (Fig. 3).
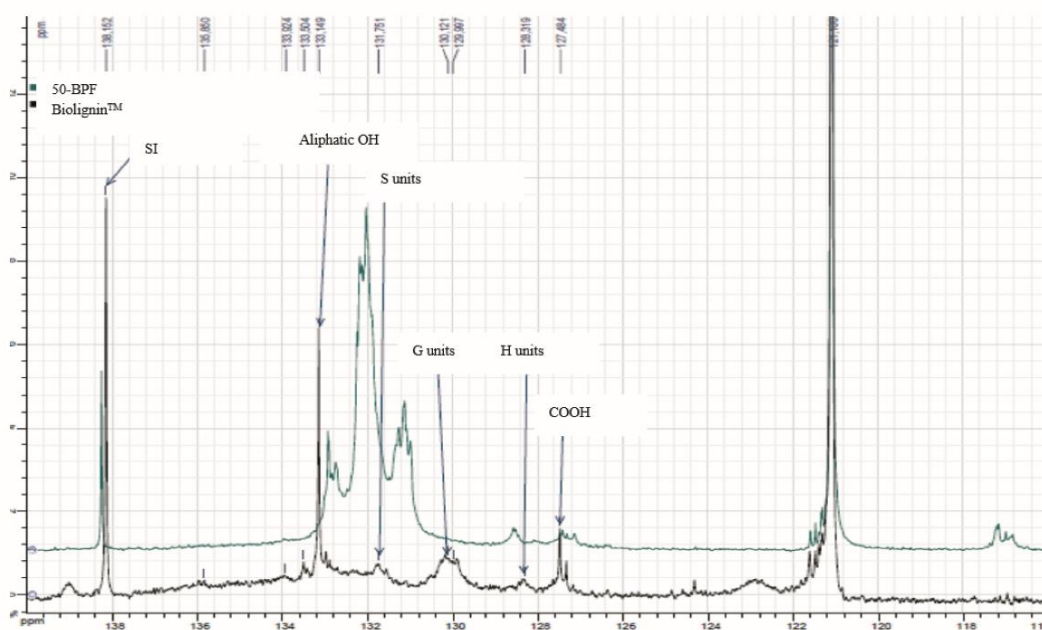
Fig. 3. ^{31}P-NMR of native BL compared with ^{31}P-NMR of BL-phenol-formaldehyde resin

The resulting resin was homogeneous. In the ^{31}P-NMR spectrum, no peak was detected around 130 ppm, corresponding to the chemical shifting of uncondensed guaiacyl units of BL. Guaiacyl units have at most one free *ortho* position that is a predicted site of reaction for formaldehyde. The ^{31}P-NMR analysis confirmed that BL guaiacyl units reacted during the resin synthesis as a source of phenol groups, and not simply as filler. Consequently, BL could be used as a phenol source to produce phenolic resins. To reach the specific properties for such a resin with a high phenol substitution rate, the BL-based resin synthesis was optimized.

Influence of Phenol Substitution Rate on Resin Characteristics

For each substitution rate, the quantity of added water was adjusted to the required resin dry matter, and the amount of sodium hydroxide was adjusted to the required pH value. The formaldehyde-to-phenol source mass ratio was maintained at the value of the commercial resin formulation PFref (64%).

Different amounts of phenol were substituted with BL. Water addition, sodium hydroxide ratio and reaction time were adapted to satisfy the dry matter, pH, and viscosity requirements listed in Table 3. The mass ratio of sodium hydroxide-to-phenol sources was increased from 22% for PFref to 25% for BL; Table 4 shows the resin characteristics of commercial PFref and 4 BPFs synthesised using different BL contents. The mass ratio of formaldehyde-to-phenol sources for each synthesis was the same as the standard ratio at 64%. With this formulation, it was impossible to prepare a 70% substituted resin. The water content of the mixture was too high to maintain 44% of resin dry matter.

Table 4. Characteristics of PF and BPF Synthesized at Different Phenol Substitution Rates

Sample	% of BL (% in total phenol sources)	Reaction Time (min)	pH	Viscosity at 20°C (P)	Dry Matter (%)
PFref	0		12	5.0	45
20-BPF	20	45	11.6	4.2	47
30-BPF	30	35	11.7	4.7	47
50-BPF	50	20	11.8	7.3	47
60-BPF	60	12	11.8	6.3	46

Over 90 °C, the condensation of newly formed hydroxymethylphenol occurs. Reaction time was defined as the time the temperature of the mixture stayed over 90 °C. During this time, the reaction temperature would reach 100 °C, which was the optimal temperature of the reaction. The reaction time affects the condensation degree of the resin and thus the resin viscosity. To satisfy the requirements listed in Table 3, especially for viscosity, the reaction time had to be adapted for each of the BL contents.

One oligomer of lignin is composed of around 8 phenolic monomer units linked together (Table 1). A greater substitution of phenol with BL required a shorter reaction time. With this adjustment for phenol substitutions between 0 and 60%, all of the synthesised resins achieved the viscosity, dry matter, and pH requirements (Tables 3 and 4). Considering lignin structure, besides reducing reaction time, a lower quantity of formaldehyde is needed since 8 phenolic monomers are already linked together in BL (Fig. 2). However, reducing the reaction time might have also influenced the formaldehyde consumption and the residual free formaldehyde content in the resin. Thus, free residual formaldehyde was measured in each resin (Fig. 4).

When no more than 30% of phenol was substituted by BL, the residual free formaldehyde remained under the critical value of 1%. When the quantity of BL exceeded this value, some formaldehyde was consumed, but the residual free formaldehyde increased dramatically towards an unacceptable value. Thus, at > 30% BL content, the formaldehyde-to-phenol sources ratio had to be decreased.

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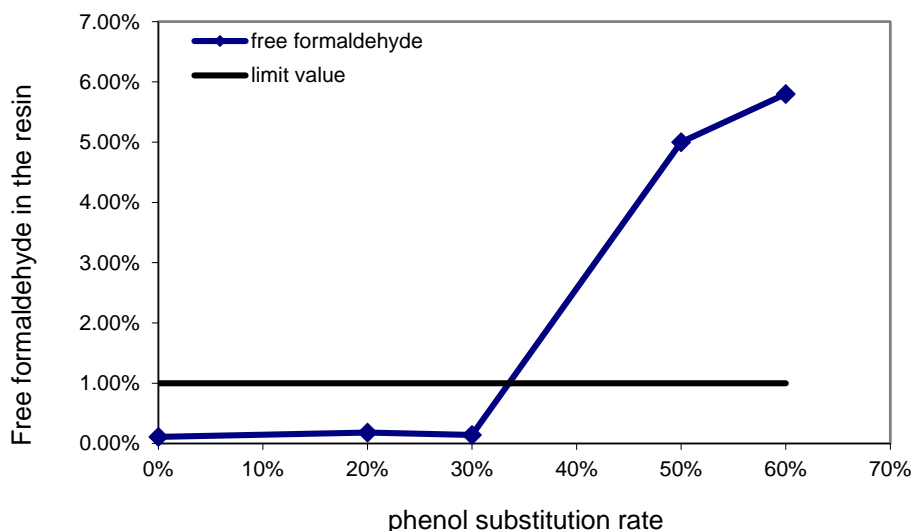
**Fig. 4.** Residual free formaldehyde content according to phenol substitution rate

Reaction times of 20 min and 12 min were the optimal times for 50-BPF and 60-BPF, respectively, to satisfy almost all requirements. However, there was more than 5% residual formaldehyde remaining for both. Due to an initial formaldehyde-to-phenol mass ratio of 64%, residual free formaldehyde and viscosity requirements could not be reached simultaneously.

Formaldehyde reacts with the unsubstituted *ortho* and *para* positions of phenolic groups. After this electrophilic addition, the newly formed hydroxymethylphenol condenses. In BL, all *para* positions are substituted. The number of free *ortho* positions depends on the number of guaiacyl and *p*-hydroxyphenyl units in the BL backbone. No *ortho* position is free in syringyl units. There are one in uncondensed guaiacyl units and two in uncondensed *p*-hydroxyphenyl units. Those units have been quantified by ^{31}P-NMR (Table 2). Then the number of active site for electrophilic addition to formaldehyde could be evaluated. A maximum of 1.2 mmol of formaldehyde can undergo an electrophilic addition with phenolic monomer units per gram of BL, whereas a maximum of 31.9 mmol of formaldehyde can react with 1 g of phenol.

The chemical structures of phenol and BL indicate that less formaldehyde is required to saturate all the free positions in BL than in phenol; thus, the initial ratio of formaldehyde must be decreased when BL is used. Moreover, the reactivity of the free sites of BL may differ from those of phenol free sites, due to steric hindrance and intrinsic chemical structure (Banoub *et al*. 2007). Both the consumption of formaldehyde in a BL and phenol media and the optimal initial ratio of formaldehyde were evaluated.

Influence of Reaction Time on the Consumption of Formaldehyde

The consumption of formaldehyde during the reaction was studied for 50-BPF and 60-BPF resins (Fig. 5). At a reaction time of 0, when the temperature reached 90 °C, 26% of formaldehyde had been consumed regardless of whether the substitution rate was 50% or 60%. Afterwards, the formaldehyde consumption increased asymptotically during the reaction. The final consumption was lower for 60-BPF than for 50-BPF.
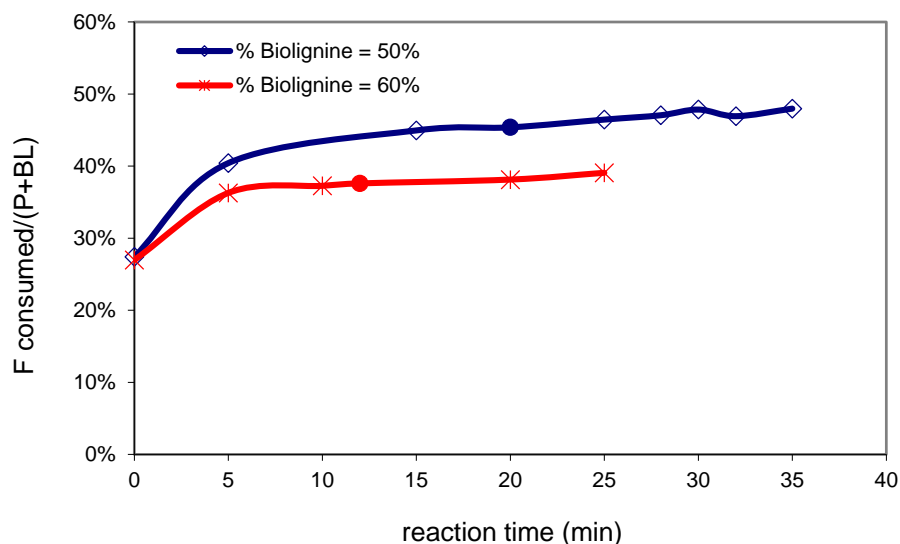
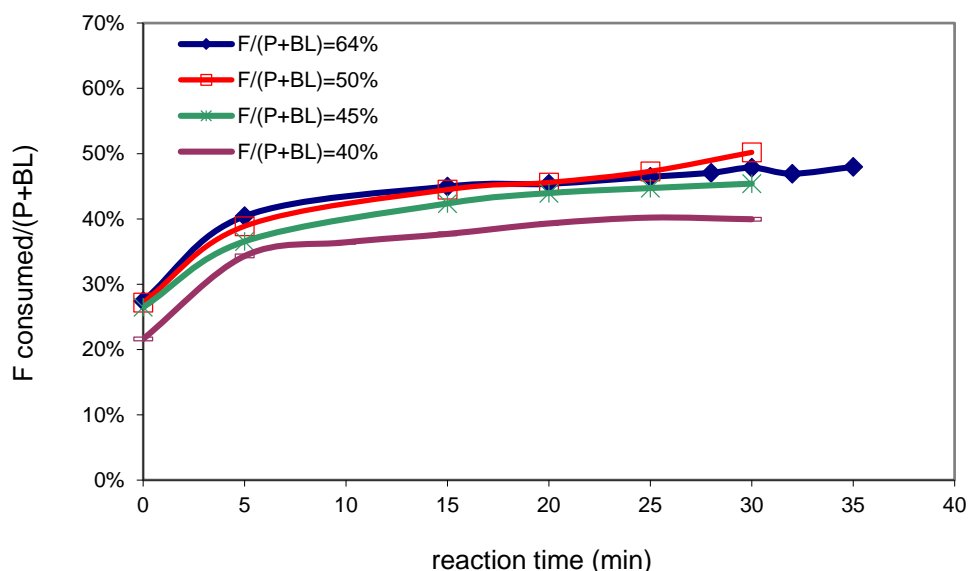**Fig. 5.** Consumption of formaldehyde during synthesis of 50-BPF and 60-BPF

No more than 45 to 48% of formaldehyde was consumed during 50-BPF synthesis, and this value was reached after 25 min of reaction time. No more than 40 to 42% was consumed during 60-BPF synthesis, and this value was reached after 15 min. For both resins, when the limit value was reached, the resin viscosity continued to increase until eventually caking after 30 to 35 min. After this point, the two resins were no longer water-soluble. This observation confirmed the results of earlier studies and underlined the fact that the reaction of formaldehyde in the aromatic cycle is faster than hydroxymethylphenol condensation to form oligomers (Mansouri 2007; Pilato 2010).

During 50-BPF synthesis, no more than 0.45 to 0.48 g of formaldehyde per gram of phenol sources was consumed, whereas at least 0.64 g of formaldehyde was consumed per gram of phenol in standard resin. Moreover, Fig. 5 shows that increasing the reaction time did not increase formaldehyde consumption above a maximum consumption value. As mentioned previously, when considering the BL chemical structure a maximum of 1.2 mmol of formaldehyde can react with 1 g of BL, and a maximum of 31.9 mmol of formaldehyde can react with 1 g of phenol. Theoretically, when 50% (w/w) of phenol is substituted using BL, a maximum of 0.496 g of formaldehyde can react with 1 g of phenol. For 60-BPF, 0.405 g of formaldehyde can react with 1 g of (phenol + BL). These considerations confirm the maximal mass ratio of formaldehyde-to-phenol sources that were previously observed. Increasing reaction time did not prompt more formaldehyde consumption because the limit was reached. In other words, all of the reactive and reachable sites of phenol sources were saturated. The initial quantity of formaldehyde was then optimised.

**Optimisation of the Initial Quantity of Formaldehyde**

Four 50-BPF resins were synthesised using formaldehyde-to-phenol sources mass ratios varying from 40% to 64%. The consumption of formaldehyde during reaction time was recorded (Fig. 6). For a F/(P+BL) ratio of 40%, the total consumption of formaldehyde was completed after a reaction time of 20 min; for a ratio F/(P+BL) of 45% it was complete after 25 min of reaction. After 25 min, there was no formaldehyde remaining in the resin. For higher ratios (50% and 64%), the consumption of formaldehyde was asymptotic. The

majority of formaldehyde was consumed during the first 15 min. Beyond 20 min of sustained reaction, formaldehyde consumption evolved very slowly and rapidly approached the maximum value. After 25 min, formaldehyde was no longer consumed. The critical ratio of formaldehyde-to-phenol sources was then confirmed as 45% to 48%. A 50% phenol substitution using BL involved a decrease of the initial mass ratio of formaldehyde from 64% to between 45 and 48%.

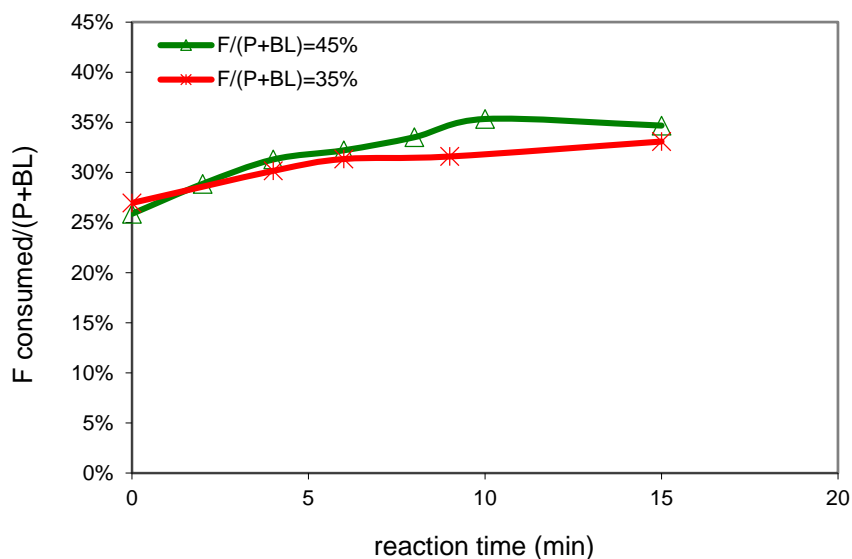**Fig. 6.** Formaldehyde consumption during 50-BPF synthesis with varied formaldehyde initial ratio

The same study was conducted for a phenol substitution rate of 60%. Figure 7 shows that no more than 40% of formaldehyde was consumed when substituting 60% of phenol with BL. A 60% phenol substitution with BL involved a decrease of the initial mass ratio of formaldehyde from 64% to 40%.
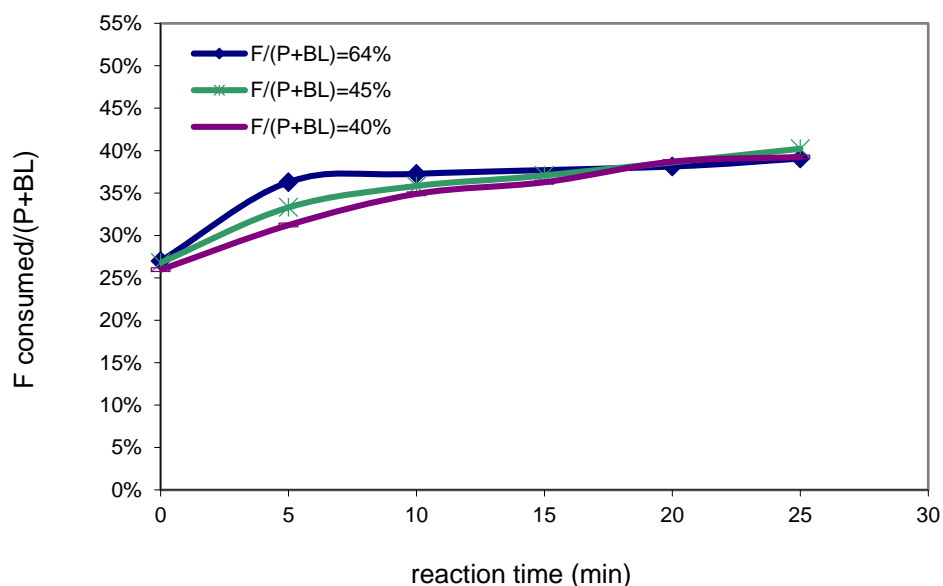
Fig. 7. Formaldehyde consumption during 60-BPF synthesis with varied formaldehyde initial ratio

With any substitution, the limit of formaldehyde consumption was reached at a reaction time longer than the reaction time required to reach the desired resin viscosity. To satisfy the viscosity requirements, the reaction was stopped before the asymptotic value of F/(P+BL) was reached, respecting the critical value of formaldehyde ($<$ 1% in the resin). An optimized resin formulation was found with a formaldehyde-to-phenol source mass ratio of 45% and 40% for 50-BPF and 60-BPF, respectively.

Increasing the phenol substitution rate involved decreasing the initial ratio of formaldehyde. Decreasing the initial quantity of formaldehyde implied a decrease in water content, which was a major obstacle in overcoming a 60% phenol substitution using the standard protocol. Two 70% substituted resins were synthesised, and the formaldehyde consumption was analysed in relation to reaction time (Fig. 8).

Fig. 8. Formaldehyde consumption during 70-BPF synthesis with varied formaldehyde initial ratio

Table 5. Operational Parameters and Characteristics of Resin

	Formulation of the commercial resin	Optimized formaldehyde ratio formulation		
Name	PF$_{ref}$	50-BPF-1	60-BPF-2	70-BPF-3
BL /(P+BL)	0%	49.9%	59.9%	69.7%
F/(P+BL)	64%	45%	41%	35%
NaOH/(P+BL)	22%	25%	25%	24%
Reaction time		20 min 30	12 min 30	5 min
Dry Matter	44.5%	48.1%	47.6%	43.5%
pH	12.4	11.7	11.6	12.1
Viscosity (20°C)	5.0 P	6.5 P	4.4 P	6.6 P
% free formaldehyde	0.07 %	0.3%	1.0%	1.0%
F consumed/(P+BL)	64%	43.8%	37.8%	31.3%

The 70-BPF obtained after 15 min of reaction was perfectly homogeneous. Between 50 °C and 90 °C, 26% of the formaldehyde was consumed. The same amount of formaldehyde was consumed at this stage during the synthesis of 50-BPF and 60-BPF.

Additionally, only 8% of the formaldehyde was consumed during the reaction time when the temperature was over 90 °C. The limit ratio F/(P+BL) tended to be 35% (Fig. 8). Theoretically, considering the number of free *ortho-para* positions in this formulation, a maximum amount of 31 g of formaldehyde was able to react with 100 g of the BL-phenol (70/30) mixture. The predicated values were of the same order of magnitude as the limit ratio.

Having optimized the different reaction parameters (Table 5), the corresponding resin satisfied standard specifications.

The viscosity requirement limited the reaction time of 70-BPF synthesis to 5 min. Increasing the substitution led to a decrease in the reaction time. When this occurred, the reaction became too short, and the reaction could not be controlled. Hence, substituting 70% of phenol with BL using the implemented protocol was the highest substitution rate that could be reached, with the limiting parameter being reaction time.

Characterization and Application of Substituted Resins

The PFref, 50-BPF-1, 60-BPF-2, and 70-BPF-3 resins were totally homogeneous and met the specifications of pH and viscosity. PFref presented a slightly high but acceptable pH. Similarly, 70-BPF-3 presented a slightly low dry matter, which was acceptable for applications in wood adhesives. Considering the resins obtained using optimized formulation (50-BPF-1, 60-BPF-2 and 70-BPF-3), there was still some formaldehyde remaining in the resin, but the amount satisfied the requirement (< 1%) indicated in Table 3. Table 6 and Fig. 9 present the DLTMA results for the three optimized substituted resins and a commercial PF.

Table 6. DLTMA Characteristics for Substituted BPF Resins and Standard PF

	PF	50-BPF-1	60-BPF-2	70-BPF-3
E_{max} (MPa)	1540	1575	1520	1490
T onset (°C)	123	126	127	126
T endset (°C)	139	138	139	141
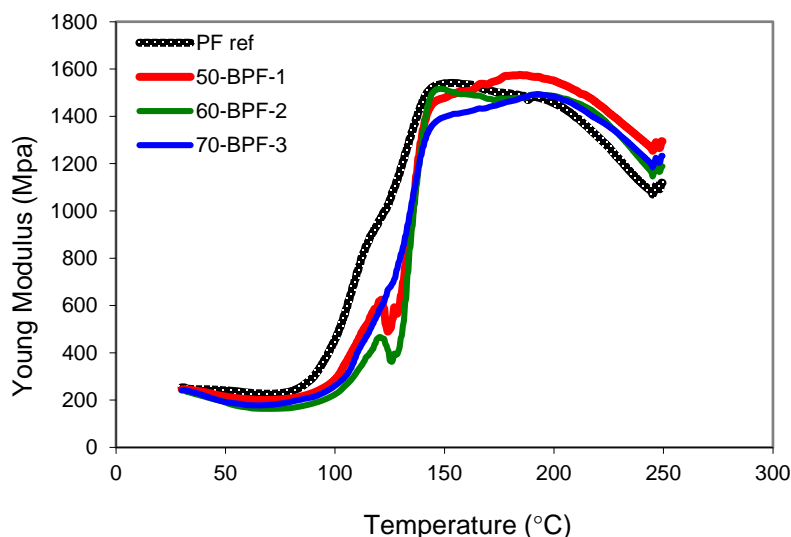
Fig. 9. DLTMA of 50-BPF-1, 60-BPF-2, and 70-BPF-3 resins compared with standard PF

The three curves obtained from the 50-BPF-1, 60-BPF-2, and 70-BPF-3 resins nearly overlapped, indicating that their onset temperature, maximum Young modulus, and curve form were close. From a thermo-mechanical point of view, crosslinking of PF and LPF resins seemed to be independent from the substitution degree. When comparing the 3 curves to the PFref curve, maximal Young modulus of all the substituted resins were close to that of PFref. The gaps between the Young modulus were not significant when they were less than 100 MPa. These results underlined the good quality of the adhesive joint. There was a difference of 3 °C between the crosslinking temperature of PFref and BPF (T_{onset} PFref < T_{onset} BPF). This effect was attributed to the final step of formaldehyde consumption, which postponed the crosslinking reaction. When used as wood adhesives, the slight delay in the beginning of the crosslinking reaction would be overcome by a slight elongation of the pressing time or by a slight increase in pressing temperature. The resins 50-BPF-1, 60-BPF-2, and 70-BPF-3 satisfied the industrial requirements and showed values of thermo-mechanical properties high enough to be tested in a wood adhesive application.

Application in Plywood Adhesives

As the three resins presented properties close to those of standard PF, they were tested as plywood panel adhesives. The criterion of conformity relating to shear strength and cohesive failure are reported in Table 7.

Table 7. Criterion of Conformity of a Plywood Panel (Mansouri 2007)

Shear Strength (N/mm²)	Cohesive Wood Failure (%)
0.2-0.4	80
0.4-0.6	60
0.6-1.0	40
>1.0	none

Table 8 presents the shear strength and cohesive wood failure results for five-ply plywood panels manufactured from 50-BPF-1, 60-BPF-2, 70-BPF-3, and PFref. All panels met the CTB X requirements presented in Table 7 and were in accordance with the criterions of use.

Table 8. Characterization of Plywood Prepared with Various Resins

Sample	Shear Strength (N/Mm²)	Cohesive Wood Failure (%)	Formaldehyde (mg/100 g of dry panel)
PF$_{ref}$	1.42	68	0.9
	1.66	82	
50-BPF-1	1.58	40	1.8
	2.25	20	
60-BPF-2	1.76	26	1.8
	1.63	54	
70-BPF-3	1.72	20	1.5

The formaldehyde content of the panel was lower for the panel containing a standard PF resin adhesive than it was for the panel containing BL-based resin. However, all four panels resulted in formaldehyde content less than 8 mg/100 g of dry panel, which places them in the E1 class (Mansouri 2007). Moreover, the formaldehyde content was even less than 4 mg/100 g, the level fixed by the severest legislation in the world (Labat and Gaillard 2013). In sum, using the 50-BPF, 60-BPF, and 70-BPF resins as plywood adhesives resulted in high quality panels that satisfied the application criteria.

CONCLUSIONS

1. Organosolv lignin extracted using the CIMV process™ was successfully used as a green phenol to produce bio-based phenolic resin without any prior chemical modification. The organosolv lignin selected, BL, easily substituted 70% (w/w) of the phenol. The rate of 70% was identified as a limit of substitution of phenol using BL.

2. Adapting the reaction time of resin synthesis, the substituted resins satisfied the industrial requirements (dry matter, pH, and viscosity) for wood adhesives without major modifications of the industrial protocol.

3. The formaldehyde-to-phenol source ratio was decreased from 64% in PFref to 35% in 70% BL-based PF resin. BL acted as a pre-polymer whose structure is comparable to the formo-phenolic resin network. This characteristic allowed for the decrease in formaldehyde.

4. The resulting BL-based PF resin achieved the specifications of PF resin in terms of dry matter, pH, and viscosity. Moreover, the residual free formaldehyde content was < 1%, as required. The industrial protocol was not changed.

5. The BL-based resins were tested using dynamic load thermo-mechanical analysis. The results were close to the standard PF resin. Their use in plywood gave rise to panels that reached conformity, with a limited content of formaldehyde in total accordance with every international regulation.

6. Given the satisfactory results, the preparation and use of BL-based resins in particle boards and plywood panels is under validation on an industrial scale.

7. This report is a decisive scientific, technical, and economical breakthrough that for the first time opens the way to a massive industrial use of unmodified lignin in phenolic resins on an industrial scale.

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