

Environmentally Friendly Mixed Tannin/Lignin Wood Resins

Hong Lei,^{1,2} A. Pizzi,¹ Guanben Du²

¹ENSTIB–LERMAB, University of Nancy 1, 27 Rue du Merle Blanc, F-88000 Epinal, France

²Southwest Forestry College, Kunming, Yunnan, People's Republic of China

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ABSTRACT: We obtained lignin-based wood adhesives satisfying the requirements of relevant international standards for the manufacture of wood particleboard. These were based on two different low-molecular-mass lignins. These lignin-based wood adhesives did not use any formaldehyde in their formulation; formaldehyde was substituted with a nonvolatile nontoxic aldehyde, namely, glyoxal. The last formaldehyde present, contributed by a fortifying synthetic phenol–formaldehyde resin, was also eliminated by the substitution of the phenol–formaldehyde resin with a natural,

vegetable polyflavonoid tannin extract to which no aldehyde was added. This substitution brought the total content of natural material up to 80 wt % of the total adhesive. The adhesives yielded good internal bond strength results of the panels, enough to pass relevant international standard specifications for interior-grade panels. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 203–209, 2008

Key words: resins; adhesives; thermosets; structure property relations; biopolymers

INTRODUCTION

Lately, there has been considerable industrial interest in the development of natural, or green, wood adhesives to substitute for synthetic thermosetting resins as adhesives for wood panels because of an undue increase in the cost of oil and mounting environmental pressure worldwide. A number of different approaches have been investigated, namely, the use of soy protein adhesives,^{1,2} the upgrading of vegetable tannin adhesives to formulations without aldehydes or even without hardeners^{3,4} and more recently, the development of polycondensation products of glyoxalated lignin (GL) with phenol–formaldehyde (PF) resins and isocyanates [(polymeric 4,4'-diphenyl methane diisocyanate (pMDI)).⁵ The abundance of lignins of different types as waste products in pulp mills has made such materials an attractive proposition for the preparation of adhesives ever since the pulping of wood to produce paper. The literature on the use of lignins to prepare wood adhesives is very extensive, and good reviews of it exist.^{6–12} In contrast to the great number of articles regarding its utilization, the record of its industrial use for wood adhesives is instead rather poor.

In the approach of adhesive formulations based on the polycondensation products of GL with PF resins

and isocyanates (pMDI),⁵ up to 55–60% of lignin was used on total resin solids. The rest of the material was composed of a mix of PF resins and isocyanates. The system was based on the reaction of polymeric isocyanate (pMDI) with pre-methylolated or preglyoxalated lignin, to which about 20% of a PF resole resin was added. It crosslinked both through the formation of lignin–lignin, lignin–phenol, and phenol–phenol methylene bridges and by the formation of urethane bridges between the hydroxymethyl groups on pre-reacted lignin and PF resin with the isocyanate, with these latter types of crosslinking in the majority. Lignin-based wood adhesives satisfying the requirements of relevant international standards for the manufacture of interior-grade and exterior-grade wood particleboard, in which formaldehyde was not used in the preparation (it was substituted by a nonvolatile nontoxic aldehyde, namely, glyoxal) were prepared and tested for application to wood panels, such as particleboard. Glyoxal is a nontoxic aldehyde [median lethal dose (LD₅₀) for rats ≥ 2960 mg/kg; LD₅₀ for mice ≥ 1280 mg/kg]¹³ and is nonvolatile but less reactive than formaldehyde, which is toxic (LD₅₀ for rats ≥ 100 mg/kg; LD₅₀ for mice ≥ 42 mg/kg).¹⁴ These adhesive systems worked well; panels of good strength were obtained at industrially significant short pressing times.⁵ In the search to further increase the proportion of natural, environmentally friendly materials in these formulations, we tried to eliminate the PF resin from the formulations and to substitute these with vegetable polyflavonoid tannins.

Correspondence to: A. Pizzi (pizzi@enstib.uhp-nancy.fr).

In this study, we first dealt with the optimization of lignin-based adhesives for wood by attempting to eliminate the addition of a synthetic PF resin, substituting it with a natural vegetable tannin extract. The aim then was (1) to completely eliminate formaldehyde from the adhesive and (2) to increase the proportion of natural, environmentally friendly materials in these adhesive formulations.

EXPERIMENTAL

Work on GL/PF/pMDI formulations was previously done with a calcium lignosulfonate, the molecular mass of which was drastically decreased by thermal treatment^{5,15} in a reactor at 170°C for 90 min at an initial pH of 12.7. This was done to decrease the molecular mass of the lignin and to render the material more suitable for the reaction.^{5,15} Other types of lignosulfonates, such as ammonium lignosulfonate, are generally equally suitable for the types of formulations described when formaldehyde has been used.^{16–18}

In this study, we used two types of already low-molecular-weight lignins. These were (1) a wood lignin produced in India and imported/commercialized under the name Protobind 100SA by a Swiss company and (2) an acetic acid wheat-straw lignin obtained by paper pulp from an experimental pilot factory in France. The first of these was used as delivered and after heat treatment (GLAF), as used previously for higher molecular weight lignins.^{5,15}

PF resin preparation and tannin extract

This PF resin was optimized in previous work on lignin adhesive formulations.^{16–18} It was the most suitable found in previous work^{16–18} yet was the simplest to prepare. More complex PF resins could be equally effective. A 500-mL, flat-bottom flask equipped with a condenser, thermometer, and magnetic stirrer bar was charged with 94 parts by mass phenol, a 40-part (20/80) methanol/water solution, and 55 parts by mass 96% paraformaldehyde. After stirring was conducted for 30 min at 40°C, the temperature was slowly, over a period of 30 min, increased to reflux (94°C). A total of 20 parts by mass of 33% sodium hydroxide solution was added in 4 equal parts at 15-min intervals. The mixture was refluxed for 60 min and then cooled in an ice bath to yield a pale yellow transparent resin of 750 cps and 60% solid content.

Commercial mimosa tannin extract in spray-dried, water-soluble powder form and supplied by Tanac SA (Montenegro, Brazil) was substituted for the PF resin in the mixed adhesive. The tannin was predissolved in water, and the pH was corrected with 30% NaOH solution to the same pH of the GL before it

TABLE I
Wood Particleboard Results for GL 1

	Board density (kg/m ³)	Dry IB strength (MPa)
GL 1/pMDI/mimosa tannin		
55/25/20	708	0.36 ± 0.05
55/30/15	733	0.36 ± 0.05
60/25/15	694	0.31 ± 0.05
60/40/0	674	0.46 ± 0.04
60/40/0	705	0.53 ± 0.04
GLAF55/25/20	733	0.31 ± 0.05
55/25/20	725	0.38 ± 0.09
GL 1/pMDI/PF control		
55/25/20	701	0.35 ± 0.04
55/20/25	673	0.31 ± 0.05

The tannin extract was substituted for the synthetic PF resin.

was mixed with the latter. In some thermomechanical analysis (TMA) testing cases, free glyoxal to react with the tannin was also added, but as this proved unnecessary, the tannin was added without glyoxal to the lignin for all of the wood panels made.

Glyoxalation of lignin

Lignin powder (29.5 parts by mass, 96% solid) was slowly added to 47.65 parts water, and sodium hydroxide solution (30%) was added from time to time to keep the pH of the solution between 12 and 12.5 for better dissolution of the lignin powder; this was also facilitated by vigorous stirring with an overhead stirrer. A total of 14.1 parts by mass of sodium hydroxide solution (30%) was added, which resulted in a final pH near 12.5.

A 250-mL, flat bottom flask equipped with a condenser, thermometer, and magnetic stirrer bar was charged with the previous solution and heated to 58°C. Glyoxal (17.5 parts by mass, 40% in water) was added, and the lignin solution was then continuously stirred with a magnetic stirrer/hot plate for 8 h. The solids content for all GLs was around 31%.

Another GL was prepared with different glyoxal, sodium hydroxide, and water proportions. The quantities used in the formulations are indicated in Tables I and II.

TMA

The hardening reaction of one resin system or glue mixtures can be evaluated by TMA by the study of the rigidity of the wood–resin joint as a function of temperature. Thus, different glue mixes of GLs with isocyanate (pMDI), mimosa tannin with and without glyoxal, and PF resin were thermomechanically analyzed. The composition of resin solid to resin solid for each different mix are given in the tables. All

TABLE II
Wood Particleboard Results for GL 2

	Board density (kg/m ³)	Dry IB strength (MPa)
GL 2/pMDI/PF control		
55/25/20	698	0.36 ± 0.05
55/20/25	673	0.31 ± 0.05
GL 2/pMDI/mimosa tannin/glyoxal		
55/20/25/3.5	681	0.19 ± 0.06
55/20/25	692	0.16 ± 0.05

The tannin extract was substituted for the synthetic PF resin.

experiments were conducted under the same conditions: heating rate = 10°C/min, 30 mg of resin system, and temperature range = 25–250°C. The thermomechanical analyzer was a TMA40 instrument from Mettler Toledo. The software used for data treatment was STARe (France). Deflection curves, which permitted the determination of the modulus of elasticity (MOE), were obtained in a three-point flexion mode. The MOE of wood–resin systems give a good indication of the strength of the final application of the experimental glue.

The maximum MOE value and its increase as a function of time or temperature for wood–resin systems give a good indication of the possible end performance of the adhesive system tested.

Blending of GL with tannin or phenolic resins and pMDI

The GL water solution was thoroughly mixed with either a 45% solution of mimosa tannin extract at the same pH or a synthetic PF resin with a solid content around 60%, as indicated in the tables. Only non-emulsified pMDI was used throughout. The diisocyanate raw pMDI was added before application and mixed in well. In the particleboard preparation, all glue mixtures had a pH between 11.5 and 12.

Particleboard manufacture and testing

One-layer laboratory particleboard with dimensions of 350 × 300 × 14 mm were prepared with only core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) wood mixture at a maximum pressure of 25 kg/cm² and a press temperature of 195°C. The resin solid load was maintained at 10% of the total mix of modified lignin + isocyanates, except where otherwise indicated in the tables. The total pressing time was maintained at 7.5 min. All particleboards were tested for dry internal bond (IB) strength.

Solid-state Fourier transform infrared (FTIR) spectra of the hardened UF, PF, and PUR controls and the hardened UF/PUR (70/30 and 60/40 w/w) and

PF/PUR (70/30 and 60/40 w/w) resin systems used were obtained by the preparation of KBr pills on a Shimadzu FTIR 8200 infrared spectrophotometer (Champs sur Marne, France).

RESULTS AND DISCUSSION

The initial TMA results of the curing of different GL formulations, shown in Figure 1, indicate that GL by itself gave a relatively low wood-joint strength. The use of a generally very effective accelerator of the aldehyde/phenolic polycondensation reaction, such as triacetin (glycerol triacetate), did not improve the performance of the GL resin when this was used alone (Fig. 1). The addition of a high amount of pMDI to give a 60 : 40 proportion of GL to 4,4'-diphenyl methane diisocyanate (MDI) in the formulation yielded a noticeable improvement in the maximum value of the MOE on curing of the joint (Fig. 1). The addition of triacetin accelerator, also in the case of this formulation, did not improve the performance of the resin; on the contrary, it appeared to interfere severely with its curing (Fig. 1). The substitution of the triacetin with the very reactive resorcinol further improved the performance of the formulation (Fig. 1). The improvement induced by the addition of a small proportion of resorcinol to the 60/40 GL/MDI formulation was expected; the highly reactive sites of the resorcinol in effect functioned as condensation sites of the hydroxy methyl groups of GL. The 60/40 GL/MDI and, even more, the 60/40/5 GL/MDI/resorcinol adhesives cured markedly faster, as shown by the rapid increase of strength at much lower temperatures than for the other adhesive formulations (Fig. 1).

The considerable improvement induced by resorcinol on the 60/40 GL/MDI formulation was only a technical curiosity, with no real applicability in prac-

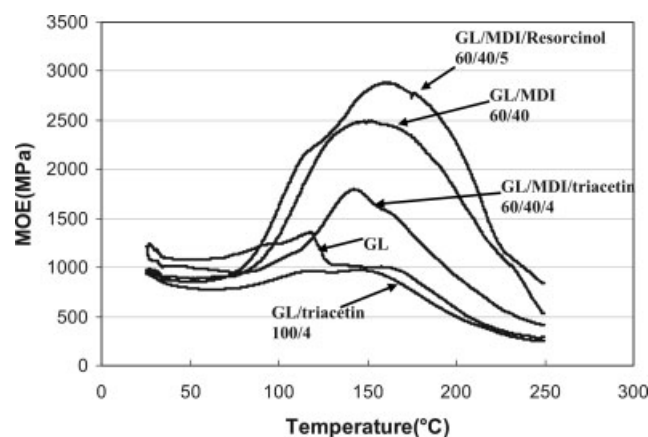


Figure 1 TMA measuring MOE as a function of temperature to describe the curing of different resins of a low-molecular-weight glyoxalated hardwood lignin.

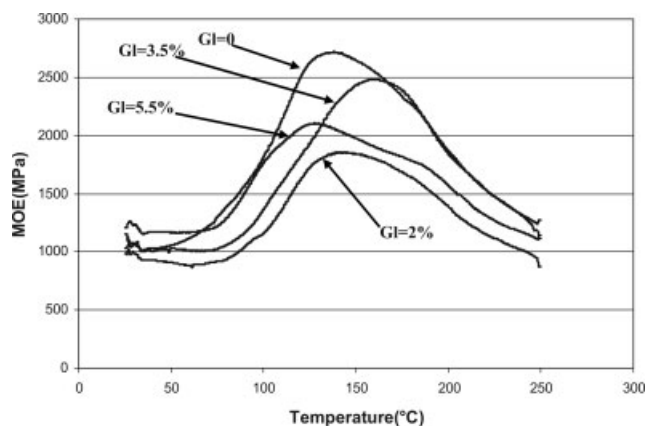


Figure 2 TMA measuring MOE as a function of temperature to describe the curing of GL/MDI/mimosa tannin when different amounts of free glyoxal were added to the glue mix. The resins were based on a low-molecular-weight glyoxalated wheat straw lignin.

tice, for three reasons: (1) the proportion of MDI (40% of the formulation on a resin solids basis), which is relatively expensive, was still relatively high, (2) one should try to increase the proportion of natural material, and (3) resorcinol is far too expensive to be used as such, even in small proportions, for a thermosetting wood panel adhesive. However, polyflavonoid tannins have reactivities with aldehydes comparable to that of resorcinol,¹⁹ and natural tannin extracts are inexpensive. We then tried to add a polyflavonoid tannin to the formulation in place of resorcinol. As shown in Figure 2, a basic adhesive formulation composed of GL/MDI/tannin extract showed a comparable performance to the resorcinol-added formulation but with the added advantage that the proportion of MDI was decreased to 20% of the total when 25 wt % was tannin extract. The highly reactive sites of the tannin functioned as condensation sites of the hydroxy methyl groups of GL just as resorcinol did for the best adhesive, shown in Figure 1. The advantages of this adhesive formulation were a much lower proportion of isocyanate (20% instead of 40%) and a greater proportion of natural materials, namely, GL plus vegetable tannin extract, for a total of 80%. The addition of a further amount of glyoxal in the glue mix, on the basis of the known reactivity of polyflavonoid tannins with glyoxal,²⁰ did not improve the performance of the adhesive and the joint (Fig. 2). Such an addition of glyoxal in the glue mix quite apparently changed the reaction mechanism of the adhesive system, with the maximum MOE value being observed for 3.5% free glyoxal added and the performance worsening at both higher and lower proportions of glyoxal in the formulation (Fig. 2). What was definite was that no addition of free glyoxal still gave the best result; this

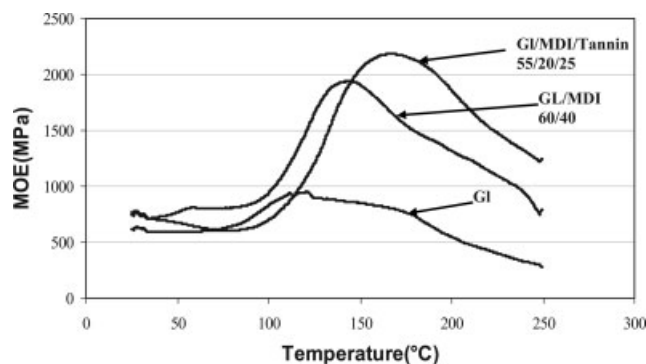


Figure 3 TMA measuring MOE as a function of temperature to describe the curing of different resins of a low-molecular-weight glyoxalated wheat straw lignin. GL with and without additives.

reproduced what was observed for resorcinol (Fig. 1). The same tendency is shown in Figure 3 for the second type of lignin, with the formulation based on 55/20/25 GL/MDI/tannin giving the best results, which were, again, slightly better than those of the GL/MDI 60/40 adhesive formulation. However, the maximum MOE values obtained with the formulations based on the second lignin in Figure 3, wheat-straw lignin, appeared to be lower than those observed in Figure 2. This means that, notwithstanding that both the lignins used were of low molecular weight, differences between each source of lignin induced a slightly different performance in the adhesives prepared with them.

As shown in Figure 2, although the 55/20/25 GL/MDI/tannin adhesive formulation was the faster curing formulation, as shown by the rapid increase of strength at much lower temperatures than for the other adhesive formulations in the same figure, the 55/20/25/5.5 GL/MDI/tannin/glyoxal with an extra free glyoxal added was also equally fast, which indicated that the lower value of maximum MOE

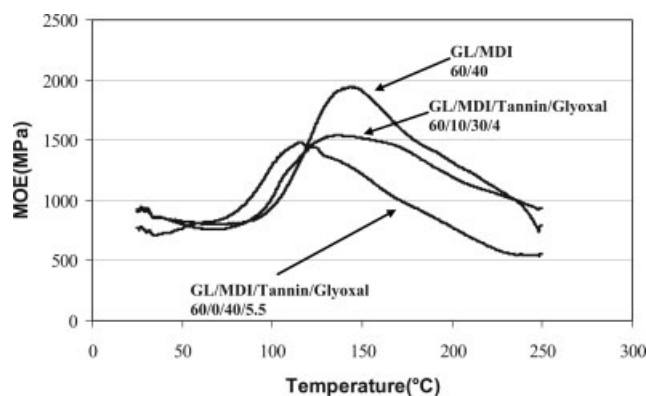


Figure 4 TMA measuring MOE as a function of temperature to describe the curing of different resins of a low-molecular-weight glyoxalated wheat straw lignin.

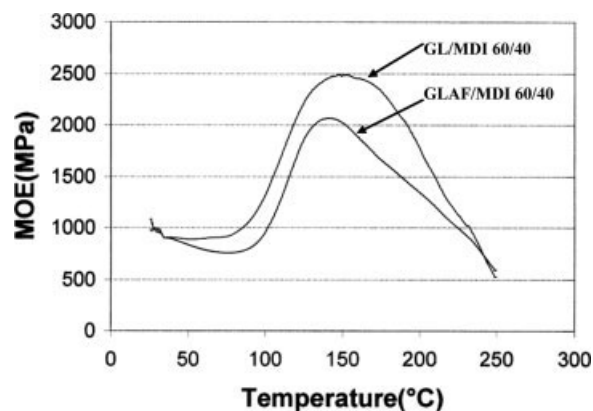


Figure 5 TMA measuring MOE as a function of temperature to describe the curing of different resins of a low-molecular-weight glyoxalated hardwood lignin. GL to GLAF difference.

obtained was due to early immobilization of the resin on curing due to the excess of glyoxal added.

In Figure 4 are reported the results of the TMA of resins in which the relative proportion of MDI was further decreased, namely, the 60/10/30 GL/MDI/tannin and 60/0/40 GL/MDI/tannin, with free glyoxal added at 4 and 5.5%, respectively. The results are clearly worse than those of the 55/20/25 GL/MDI/tannin formulation. Thus, with this type of lignin adhesive, although the addition of the very reactive tannin allowed a marked decrease in the proportion of MDI, it did not appear that MDI could be eliminated completely. However, the curve of 60/0/40/5.5 GL/MDI/tannin/glyoxal without

MDI, shown in Figure 4, showed no decrease in the maximum MOE value in relation to the curve containing 10 parts MDI, but it started curing at a lower temperature; hence, this resin cured faster. Tannin are known to considerably accelerate the curing and setting of any aldehyde-based polycondensation systems, and this could have been the case here, too. If this is so, the lower strength of the formulation may well have been due to early immobilization of the hardened network, and the formulation would have then behaved differently and with better performance once a wood panel was manufactured with it.

The application of the heat and pressure treatment, as found in the literature,¹⁵ also did not appear to improve the performance as adhesives of lignins already of fairly low molecular weight, as shown in Figure 5. To understand why this appeared to be the case, a sequence of FTIR spectra were done of the original lignin, the original lignin after dissolution at pH 12.7, the lignin after heat treatment at 170°C for 90 min, and the same lignin after redissolution in an alkaline water solution. The relevant spectra are shown in Figures 6–8, respectively. If one compares Figures 6 and 7, the disappearance of the 1210- and 1270-cm⁻¹ bands indicated that the heat treatment caused a certain extent of limited depolymerization by C—O—C cleavage and demethoxylation of the original lignin. This was supported by the decrease and disappearance of the 2,880- and 1330-cm⁻¹ bands of the —CH— stretch. However, the predominance in Figure 7 of the 1130-cm⁻¹ band indicates that the β-O-4 and α-O-4 bonds were not too affected by the treatment. The disap-

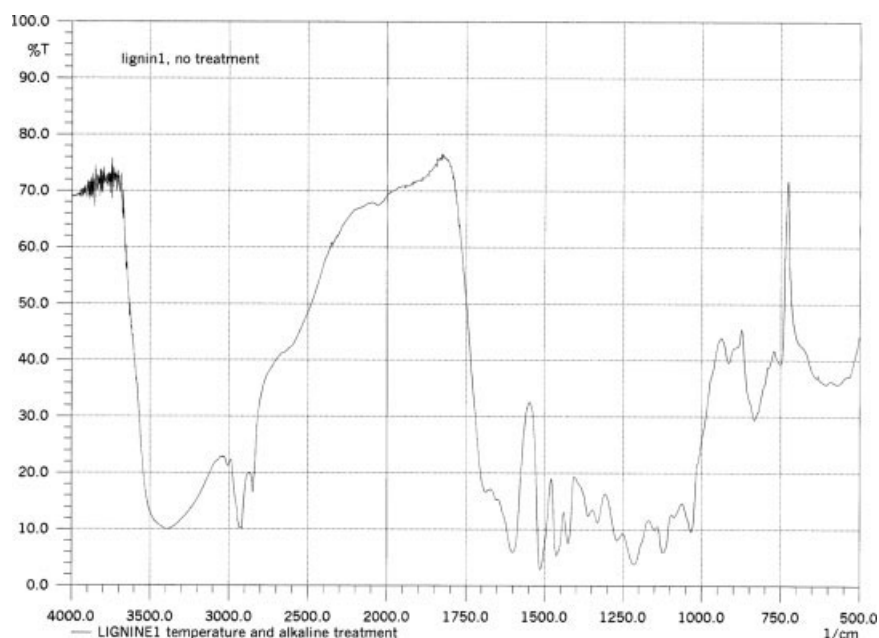


Figure 6 FTIR spectrum of an original low-molecular-weight hardwood lignin before glyoxalation.

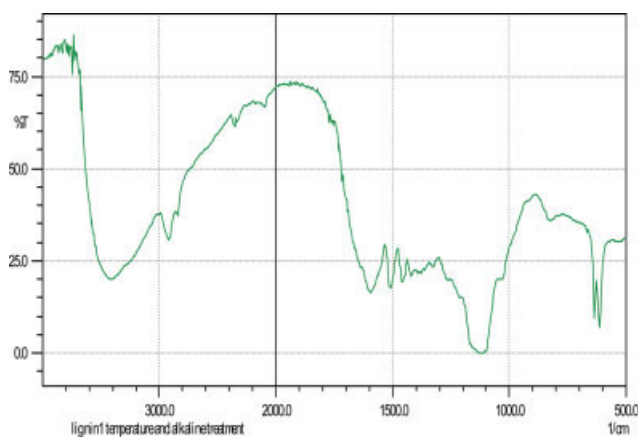


Figure 7 FTIR spectrum of a low-molecular-weight hardwood lignin after a heat treatment at 170°C for 90 min at pH 12.2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pearance of the C=O band, a C=O conjugated to an aromatic nuclei, indicated the disappearance of the —COOH and —COO⁻ groups present on the original structure. The 1,2,3,5-substitution pattern on the aromatic nuclei of lignin decrease was shown by the decrease of the 847-cm⁻¹ band. This mainly reflected the cleavage of some of the 5–5 residual bonds between lignin units. Aliphatic —CH₂OH at 1039 cm⁻¹ and β-O-β bonds at 917 cm⁻¹ were unaffected by the treatment. The relative intensities of the 1500- and 1600-cm⁻¹ peaks indicated that this was a hardwood lignin.²¹ If one compares Figures 7 and 8, the dissolution of the heat-treated material again in alkali showed other changes in the constitution of the lignin. Thus, the 1210- and 1080-cm⁻¹ bands reappeared, which indicated rearrangement and some autocondensation by the formation of (Ar)C—O—C bonds, the lignin either recovering part of the limited depolymerization observed passing from Figure 6 to Figure 7 or possibly even slightly increasing in molecular weight. This recovery indicated that the strength performance of joints bonded with the heat-treated lignin should not have been better than when the original lignin itself was used. This confirmed the results of Figure 5, where the untreated lignin formulation slightly outperformed the heat-treated one.

The FTIR in Figure 9 shows the spectrum of GL. If one compares this with Figure 6, the 1625-cm⁻¹ band characteristic of the C=O of the glyoxal disappeared, which indicated that either the aldehyde completely reacted or that its band was simply masked by the dominant and wide C=O band from lignin centered at 1600 cm⁻¹. However, that extensive glyoxal reaction had indeed occurred was confirmed by the dominance and relative increase of the band at 1420 cm⁻¹, which indicated the

increase of —CH₂—, or better —CH₂—CH₂— bridges due to the condensation reaction of glyoxal with the aromatic groups of lignin. Again, glyoxalation in a hot and alkaline environment led to the cleavage of some β-O-4 and α-O-4 bridges of lignin and to its demethoxylation, as shown by the marked decrease of the 1280- and 1230-cm⁻¹ bands. The glycol form HO—CH—OH of the aldehyde group of glyoxal in water was present (1080 cm⁻¹), which indicated that although this could be a cause of the disappearance of glyoxal's C=O signal at 1625 cm⁻¹, part of the aldehyde reactive groups were still present in the system under this form. The 1040-cm⁻¹ band of the γ —CH₂OH groups of lignin decreased markedly after glyoxalation, which indicated fairly extensive internal rearrangements of the lignin.

In Table I, we report the dry IB strength results of one-layer laboratory particleboard prepared with the previously defined resins. The results of the 55/25/20 GL/MDI/tannin resin satisfied the requirements of the relevant international standards for dry IB strength (≥0.35 MPa), whereas a decrease in MDI to 15% of the formulation appeared to decrease strength. The results of the 55/25/20 GL/MDI/tannin were comparable to those presented in the same table, in which a synthetic PF resin was used rather than tannin. The dependence of the formulation performance on the proportion of MDI is shown in the same table by the much better results of the 60/40 GL/MDI formulation, even at a relatively low panel density. The strength results of boards bonded with the heat-treated lignin (GLAF, Table I) were worse than when the original lignin itself was used. This confirmed the results shown in Figure 5 and where the untreated lignin formulation gave panels the IB strength that slightly outperformed the heat-treated one.

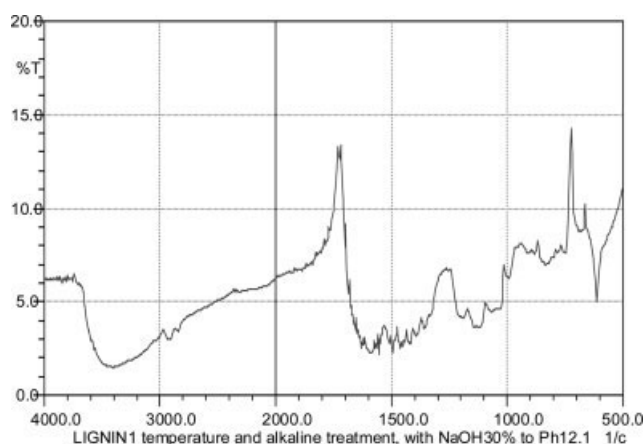


Figure 8 FTIR spectrum of a low-molecular-weight hardwood lignin after a heat treatment at 170°C for 90 min at pH 12.2 and redissolution in water at pH 12.2

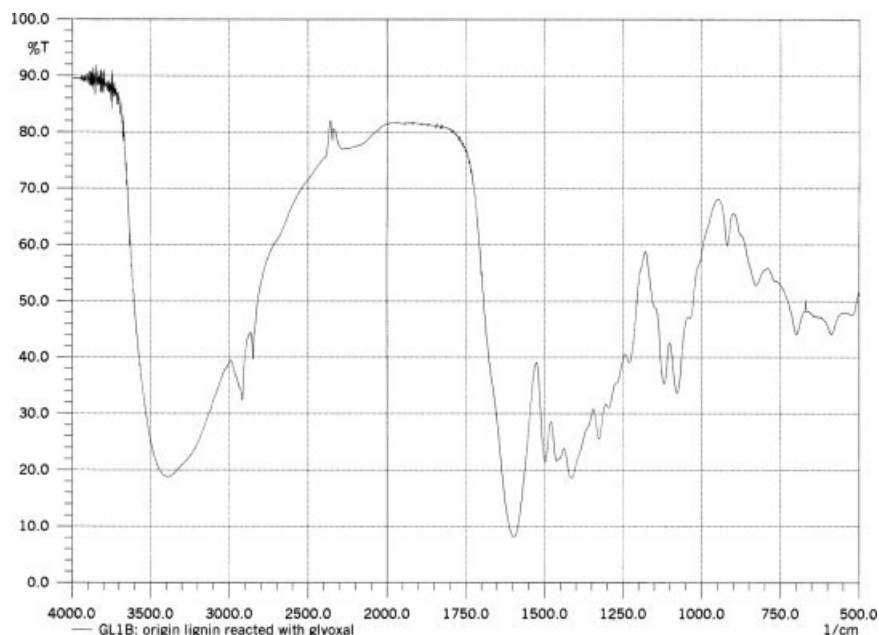


Figure 9 FTIR spectrum of a low-molecular-weight glyoxalated hardwood lignin.

Table II shows the case of another molecular weight lignin, namely, wheat-straw lignin, the results of which obtained are of the same order of magnitude and presented the same trend as observed for the first lignin.

CONCLUSIONS

The results shown in this article confirm few aspects of these fairly new tannin formulations, namely:

1. Lower molecular weight lignins appear to give better IB results than higher molecular weight lignins when MDI-based formulations are used.
2. The performance of these formulations also depends on the amount or proportion of the MDI used.
3. The IB strength results of boards bonded with the heat-treated lignin (GLAF) are worse than when the original lignin itself is used; this result was confirmed by both FTIR and TMA. Thus, the heat treatment that is so beneficial when applied to reducing the degree of polymerization of high-molecular-weight lignins in European and North American countries does not work when applied to already low-molecular-mass lignins.

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