

Lignin-Based Polycondensation Resins for Wood Adhesives

N.-E. El Mansouri,¹ A. Pizzi,² J. Salvado¹

¹Department of Chemical Engineering, University Rovira y Virgili, Tarragona, Spain

²ENSTIB-LERMAB, University of Nancy 1, Epinal, France

Received 28 February 2006; accepted 10 May 2006

DOI 10.1002/app.25098

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Lignin-based wood adhesives are obtained that satisfy the requirements of relevant international standards for the manufacture of exterior-grade wood particleboard. Formulations based on low molecular mass lignin and presenting an increase in the relative proportion of reactive points yield better results than the higher molecular mass lignin used in the past. These lignins allow a higher proportion of hydroxymethylation during preparation of methylolated lignins. These lignin-based adhesives also yield acceptable results at particleboard pressing times that are sufficiently low to be of industrial significance. Lignin-based wood adhesives, in which a nonvolatile nontoxic aldehyde (glyoxal) is

substituted for formaldehyde in their preparation, are prepared and tested for application to wood panels such as particleboard. The adhesives yield good internal bond strength results for the panels, which are good enough to comfortably pass relevant international standard specifications for exterior-grade panels. The adhesives also show sufficient reactivity to yield panels in press times comparable to that of formaldehyde-based commercial adhesives. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1690–1699, 2007

Key words: lignin; adhesives; wood; fast curing; isocyanates; glyoxal; nontoxic

INTRODUCTION

The abundance of different types of lignins as a waste product 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.^{1–7} In contrast to the great number of articles regarding its utilization, the record of its industrial use for wood adhesives is poor. There are well-documented cases of industrial processes based on lignins for wood adhesives; but because of technical, economic, process, or real availability reasons, most of these never reached industrial application or were discontinued after only a short period of use.^{1–7}

Most of the serious industrial attempts to utilize lignins for wood adhesives have been based on substituting lignin as part of phenol–formaldehyde (PF) resins or urea–formaldehyde resins. The inherently low reactivity of lignin toward formaldehyde has been partially overcome by the introduction of pre-methylolated lignin into these synthetic PF resins, thus a lignin that has been prereacted with formaldehyde. Mixes of PF resin and methylolated lignin have been used in some plywood mills. This is

possible because the rate of pressing in plywood is not the critical technical parameter determining if the process or product is economical. The situation is very different in particleboard and similar wood panels such as oriented strand board and medium density fiberboard panels, where the rate of pressing is the critical technical parameter determining the cost and profitability of both process and product.^{8,9}

A system that has been proposed since the 1990s as solving the problem of the low reactivity of lignin concentrated on introducing a further crosslinking reaction of lignin, which is independent of the reactivity limitations characteristic of a formaldehyde-based system.^{8,9} The system is based on the reaction of polymeric 4,4' diphenyl methane diisocyanate (pMDI) with pre-methylolated lignin to which small amounts of a PF resol resin has been added. It crosslinked through the formation of lignin–lignin, lignin–phenol, and phenol–phenol methylene bridges and by formation of urethane bridges between the methylol groups on lignin and the PF resin with the isocyanate, with these latter types of crosslinks in the majority. The system worked well and panels with good strength were obtained at industrially significant short pressing times.^{9,10} However, it was not optimized because of the lack of industrial interest at the time it was devised and it still needed the use of an intermediary addition of a PF resin to yield results that could be of industrial significance, especially as regards performance and a fast hot pressing rate for wood panels. This system cannot

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

be used with lignin that has not been methylolated because it has been proven that in the presence of water only the hydroxymethyl group of PF resins and methylolated lignins can preferentially react with the isocyanate group.⁸⁻¹³ Hence, any formulation variation in which lignin by itself is used in water does not work well and often not at all.

Considerable industrial interest has been shown in these systems and is developing in them today, both to try to use lignin waste material as well as to produce adhesives mainly based on more environment-friendly natural materials. An additional reason is because of the considerable increase in the price of oil-derived synthetic resins for wood adhesives in recent times. No further improvement of this approach has been pursued since the early 1990s. However, with the recent industrial interest in them, further improvements are sought.

This article describes the performance optimization of this approach to lignin-based adhesives for wood, including an attempt at the elimination of the addition of a PF resin. It also deals with attempts to substitute a nontoxic, but less reactive aldehyde for formaldehyde, because of its toxicological properties, in the modification of lignin. The aldehyde chosen was glyoxal. Glyoxal is a nontoxic aldehyde (rat LD₅₀ ≥ 2960 mg/kg, mouse LD₅₀ ≥ 1280 mg/kg)¹⁴ that is nonvolatile but less reactive than formaldehyde, which is toxic (rat LD₅₀ ≥ 100 mg/kg, mouse LD₅₀ ≥ 42 mg/kg).¹⁵ The article concludes after reaction optimization with the total substitution of a toxic carcinogenic material (formaldehyde) with a nonvolatile and nontoxic aldehyde (glyoxal) in the lignin hydroxymethylation step. The parameters of application to wood panels to achieve industrially significant fast press times are optimized while simultaneously conserving the properties of the panels to a level satisfying international standard specifications for these products.

EXPERIMENTAL

The lignin used in this work is a calcium lignosulfonate type delivered by Lignotech Iberica–Spain. It was used as readily available from industry. Other types of lignosulfonates, such as ammonium lignosulfonate, are equally suitable for the types of formulations described.^{8,9} However, the molecular mass of the calcium lignosulfonate was drastically decreased to render the material more suitable for reaction.¹⁶ This lignin was reacted in an alkaline medium at high temperature and a fine powder material was recovered from the aqueous solution by a spray drying system. The thermal treatment¹⁶ was cooking the original lignin feedstock at 170°C for 90 min at an initial pH of 12.7. Its general features are 95% dry matter, 4% ash, 66% lignosulfonate, 2.60% phenolic

hydroxyl groups, 14.5% aromatic protons, a number-average molecular weight (M_n) of 1148, a weight-average molecular weight (M_w) of 4634, a polydispersity (M_w/M_n) of 4.0, and a 55% increment in the reactive sites.¹⁶

PF resin preparation

The PF resin was optimized on lignin adhesive formulations in previous work.⁸⁻¹⁰ It is the most suitable one found in these studies,⁸⁻¹⁰ yet it is the simplest one to prepare. More complex PF resins could be equally effective. A 500-mL flat-bottom flask equipped with a condenser, thermometer, and magnetic stir bar was charged with 94 parts by mass phenol, 40 parts (20/80) methanol/water solution, and 55 parts by mass of 96% paraformaldehyde. After stirring for 30 min at 40°C, the temperature was slowly increased to reflux (94°C) over 30 min. 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 centipoises (cps) viscosity and 60% solid content.

Hydroxymethylation (methylolation) of lignin with formaldehyde

Lignin powder (29.5 parts by mass, 95% solids) was slowly added to 58.9 parts water while sodium hydroxide solution (30%) was added from time to time, thus keeping the pH of the solution between 12 and 13 for better dissolution of the lignin powder, which was facilitated by vigorous stirring with an overhead stirrer. A total of 8.1 parts by mass sodium hydroxide solution (30%) was added, which resulted in a final pH of 12.0. 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. Paraformaldehyde (3.5 parts, 96%) was added and the lignin solution was then continuously stirred with the magnetic stirrer on a hot plate for 8 h. This hydroxymethylated lignin was named MLA. In the same manner, we prepared two hydroxymethylated lignins with a great quantity of paraformaldehyde (7 and 10 parts by mass) in the same reported formulation, which we correspondingly named MLB and MLC.

Glyoxalation of lignin

Lignin powder (29.5 parts by mass, 96% solid) was slowly added to 47.65 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 with an overhead

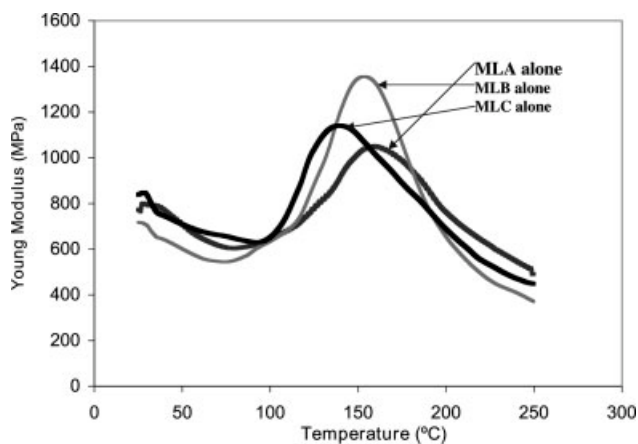


Figure 1 TMA testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to the increasing temperature and curing time when bonded with MLA, MLB, and MLC.

stirrer. A total of 14.1 parts by mass 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 stir bar was charged with the above solution and heated to 58°C. Then, 8.75 parts by mass glyoxal (40% in water) was added and the lignin solution was continuously stirred with a magnetic stirrer on a hot plate for 8 h. The solids contents for all glyoxalated lignins were around 31%.

Another glyoxalated lignin was prepared with different glyoxal, sodium hydroxide, and water proportions. The quantities used in the formulations are indicated in the following section.

Thermomechanical analysis (TMA)

The hardening reaction of one resin system or glue mixtures can be evaluated by TMA by studying the rigidity of a joint of wood resin as a function of the temperature. Thus, different glues mixes, such as methylolated lignin (ML) and glyoxalated lignin (GL; thus, MLA, MLB, MLC, and GLA, GLB, GLC), ML-pMDI, ML-pMDI-triacetin, and ML-triacetin systems and the same systems in which ML is substituted by GL, were thermomechanically analyzed. The composition of different glue mixtures is given in the following lists. All experiments were conducted at a heating rate of 10°C/min with 30 mg of resin system and a temperature range of 25–250°C. A Mettler Toledo TMA40 thermomechanical analyzer was used. The software used for data treatment was STARe. Deflection curves that permit the determination of the modulus of elasticity (MOE) were obtained in three-point bending mode. The MOE of the wood-resin system gives a good indication of the end rigidity of the final application of the glue in the experiment.

The MOE maximum 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 that was tested.

In the ML cases, a TMA of the following was performed for the percentage proportion by weight, based on resin solids:

MLA alone	MLB alone	MLC alone
MLA-pMDI (50/50)	MLB-pMDI (50/50)	MLC-pMDI (50/50)
MLA-pMDI- triacetin (50/50/17)	MLB-pMDI- triacetin (50/50/17)	
MLA-triacetin (100/23)	MLB-triacetin (100/23)	MLC-triacetin (100/23)

MLA-pMDI: 75/25 MLB-pMDI: 75/25
 MLA-pMDI: 60/40 MLB-pMDI: 60/40
 MLA-pMDI: 50/50 MLB-pMDI: 50/50
 MLA-pMDI: 43/57 MLB-pMDI: 43/57
 MLA-pMDI: 38/62 MLB-pMDI: 38/62
 MLA-pMDI: 23/77 MLB-pMDI: 23/77

Blending of methylolated or glyoxalated lignin-phenolic resins-pMDI

The methylolated or glyoxalated lignin water solution was thoroughly mixed with a phenolic resin with a solid content of around 60%, as indicated above. Only nonemulsified pMDI was used throughout. The diisocyanate raw pMDI was added before application and mixed in well. In the preparation of particleboard all glue mixtures had a pH between 12 and 12.5 for ML cases and between 11.5 and 12 for GL cases.

Particleboard manufacture and testing

One-layer laboratory particleboard (350 × 300 × 14 mm) was prepared using only core particles of a beech

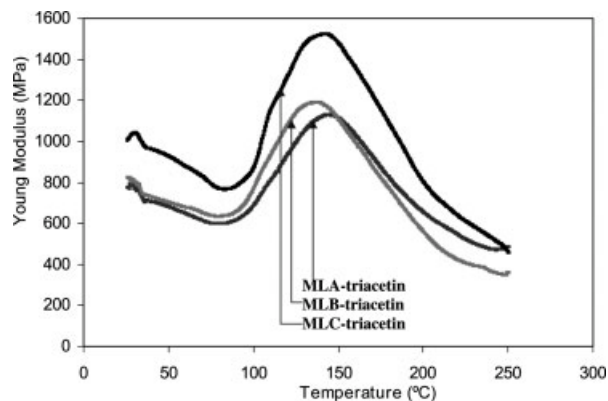


Figure 2 TMA testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with MLA-triacetin, MLB-triacetin, and MLC-triacetin. The weight ratio of ML solids to triacetin is fixed at 81 : 19.

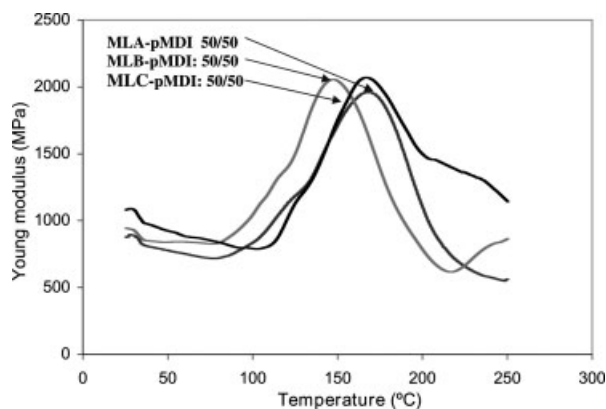


Figure 3 TMA testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with MLA-pMDI, MLB-pMDI, and MLC-pMDI. The weight ratio of ML solids to pMDI is fixed at 50 : 50.

(*Fagus sylvatica*) and Norway spruce (*Picea abies*) wood mixture at 24 kg/cm² maximum pressure and a 195°C press temperature. The resin solids load was maintained at 10% of the total mix of modified lignin plus isocyanates, except where otherwise indicated in the descriptions. The total pressing time was varied between 3.5 and 7.5 min. All particleboards were tested for internal bond (IB) strength.¹⁸ For accelerated aging tests, specimens were boiled in water for 2 h, dried at 103°C for 16 h, and tested for IB strength.

RESULTS AND DISCUSSION

The TMA results indicated that a number of resin combinations with different characteristics could be obtained. Figures 1, 2 and 3 compare the effectiveness of different levels of hydroxymethylation from the different amounts of formaldehyde prereacted

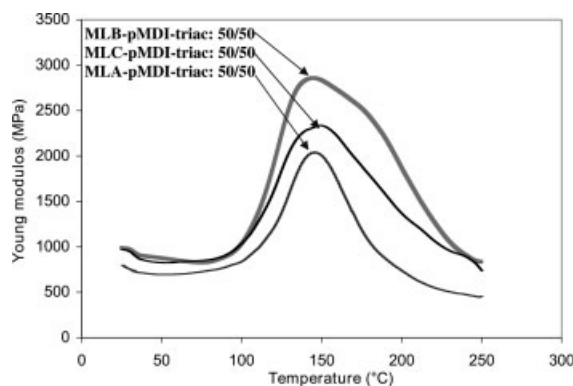


Figure 4 TMA testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with MLA-pMDI-triacetin, MLB-pMDI-triacetin, and MLC-pMDI-triacetin. The weight ratio of ML solids, pMDI, and triacetin is fixed at 50 : 50 : 8.

with lignin in the reactor. Figure 1 shows that there is an optimum proportion of formaldehyde to be added during hydroxymethylation to obtain optimal resin performance. Thus, methylolated lignin B (MLB) shows the best result. Hydroxymethylating more, or less, leads to lower performance. In an earlier study, when some of the formulations were developed,^{8,9} the optimal level of hydroxymethylation was that corresponding to MLA. However, the main change is the M_n of the lignin that was used. The value is 1148 in the present study, which is relatively low, whereas for the older study it was nearly 25,000. Thus, it is evident that the optimal level of hydroxymethylation depends on the molecular mass of the lignin that is used. The lower the molecular mass is, the higher the level of hydroxymethylation allowed for best performance and the better the performance.^{8,9} The reason why the highest MOE value of MLC is lower becomes quite clear from the relative position of its MOE curve in Figure 1. The maximum MOE value is reached much earlier than in MLB. Thus, the much higher hydroxymethylation level accelerates curing of MLC. When the hardened network formation in polycondensates is too rapid, early immobilization of the network occurs, causing a lower density of crosslinking and hence lower strength.¹⁷ This is the case for MLC in Figure 1.

The relative trend in performance is different if an ester accelerator is added (Fig. 2). The rate of curing becomes more similar for the three levels of methylolated lignin but with a maximum MOE value that is progressively higher as one passes from MLA to MLB to MLC, and it is highest for MLC (Fig. 2). This is expected because triacetin is an accelerator of the reaction of hydroxymethyl groups to form methylene crosslinks in formaldehyde-based resins,^{8,9,19-21} the

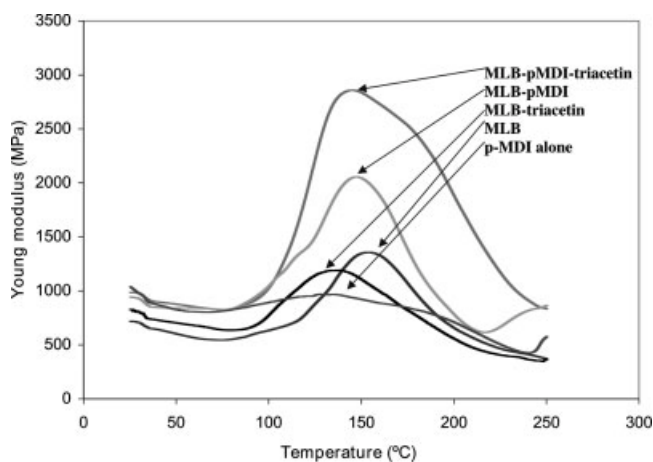


Figure 5 TMA testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with MLB, MLB-pMDI (3 and 3 g), MLB-pMDI-triacetin (50 : 50 : 8), MLB-triacetin (81 : 19), and MLA alone.

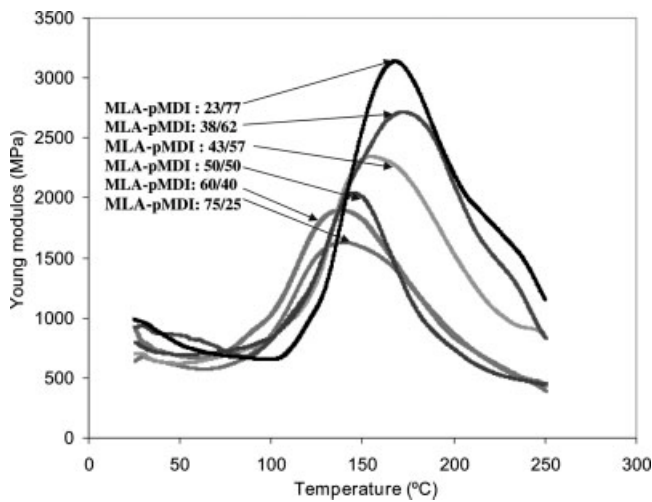


Figure 6 TMA testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with MLA-pMDI at different component ratios. The component solid weight ratios of MLA/pMDI are 75/25, 60/40, 50/50, 43/57, 38/62, and 23/77.

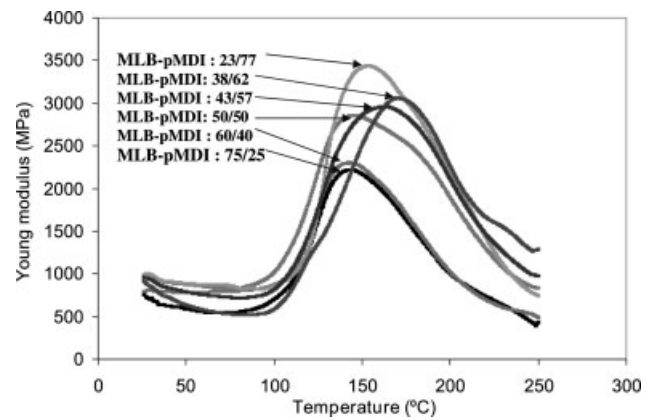


Figure 7 TMA testing of the Young's modulus of a beech wood joint as a function of adhesive hardening due to increasing temperature and curing time when bonded with MLB-pMDI at different component ratios. The component solid weight ratios of MLB/pMDI are 75/25, 60/40, 50/50, 43/57, 38/62, and 23/77.

mechanism of which has been recently reviewed in depth.²¹ It is then expected that the higher the level of hydroxymethylation of the lignin is, the higher will be the level of crosslinking obtained; hence, MLC will give a higher MOE value. The trend changes in Figure 3 where a polymeric isocyanate (pMDI) has been added. The maximum MOE value increases noticeably for all three methylolated lignins, but there is practically no difference in the maximum MOE value obtained. This is due to the crosslinking effect of the isocyanate.^{8,9,12,13} The only difference is the accelerating effect that pMDI has on MLB in relation to MLA and MLC. This may be attributable to the fact that for MLB the stoichiometry for the reaction of methylol groups with isocyanate groups is nearer to ideal. Figure 4 shows the results of the combination of methylolated lignin, isocyanate, and accelerator for the three methylolated lignins. The maximum

MOE values of all three lignins have increased, but in different amounts. MLB clearly yields the highest MOE value. This must then be considered, for the type of lignin used and its molecular mass, the best level of hydroxymethylation. Figure 5 demonstrates the progressive increase of the maximum MOE value and acceleration of cure (shown by the shift of the rising part of the curve to lower temperatures) for MLB when passing from MLB to MLB-triacetin (faster) to MLB-pMDI (stronger and faster) to MLB-pMDI-triacetin (much stronger and faster). Equivalent curves for MLA and MLC were obtained (not shown).

The effect of the relative proportion of ML and pMDI was tested in the ML/pMDI range of 75/25 to 23/77. This was done for both MLA and MLB. The results are provided in Figures 6 and 7. A comparison of the curves in Figures 6 and 7 shows that the maximum MOE value increases with the progressive increase in the relative proportion of the isocyanate

TABLE I
Effect of Different Component Ratios When Using Methylolated Lignin
(10% = Adhesive Content) on Particleboard

N	ML/pMDI/PF component ratio	Dry		Boiled for (2h)	
		Density (g/cm ³)	IB (MPa)	Density (g/cm ³)	IB (MPa)
A	75/25/0	0.710	0.423	0.714	0.098
A	60/40/0	0.699	0.724	0.691	0.273
A	50/20/25	0.698	0.567	0.722	0.196
B	75/25/0	0.687	0.484	0.680	0.133
B	80/20/0	0.687	0.405	0.693	0.123
B	55/20/25	0.710	0.697	0.700	0.214
B	60/40/00	0.703	0.823	0.724	0.292
Ct	4%	0.700	0.673	0.713	0.213
Ct	2%	0.667	0.385	0.672	0.112

Pressing time = 7.5 min. temperatures 195–200°C, thickness 14 mm.

TABLE II
Effect of Different Component Ratios When Using Methylolated Lignin 10% (Adhesive Content) on Particleboard

N	ML/pMDI/PF component ratio	Pressing time (min)	Dry		Boiled for (2h)	
			Density (g/cm ³)	IB (MPa)	Density (g/cm ³)	IB (MPa)
B	55/20/25	7.5	0.710	0.679	0.700	0.214
B	55/20/25	5.5	0.713	0.684	0.705	0.201
B	55/20/25	4.5	0.695	0.666	0.690	0.182
B	55/20/25	3.5	0.707	0.624	0.701	0.194
B	60/40/00	7.5	0.703	0.823	0.724	0.292
B	60/40/0	5.5	0.711	0.783	0.695	0.252
B	60/40/0	4.5	0.691	0.755	0.693	0.262
B	60/40/0	3.5	0.702	0.771	0.697	0.201

Triacetin, 3% for 60/40/00 and 4% for 55/20/25 on dry basis of methylolated lignin; temperatures = 195–200°C, thickness = 14 mm.

in both MLA and MLB. However, the maximum MOE value at lower percentages of isocyanate is better for MLB (Fig. 7) for the same reasons as discussed earlier for Figure 2. For example, to achieve with MLA the maximum MOE value for a 75/25 MLB/pMDI mix, one needs a 43/57 MLA/pMDI mix, which is a much higher proportion of pMDI in the case of MLA. Because the cost of lignin is low and that of the pMDI is relatively high, this means

that MLB can be used for better performance as well as at a much lower prospective cost.

Although TMA allows quick comparative scans of different systems, it also tends to exaggerate the differences between cases. It is then necessary to compare the different, most suitable formulations by applying them to their real final use, namely, the bonding of wood particleboard. Table I provides the results of a series of particleboard tests using MLA

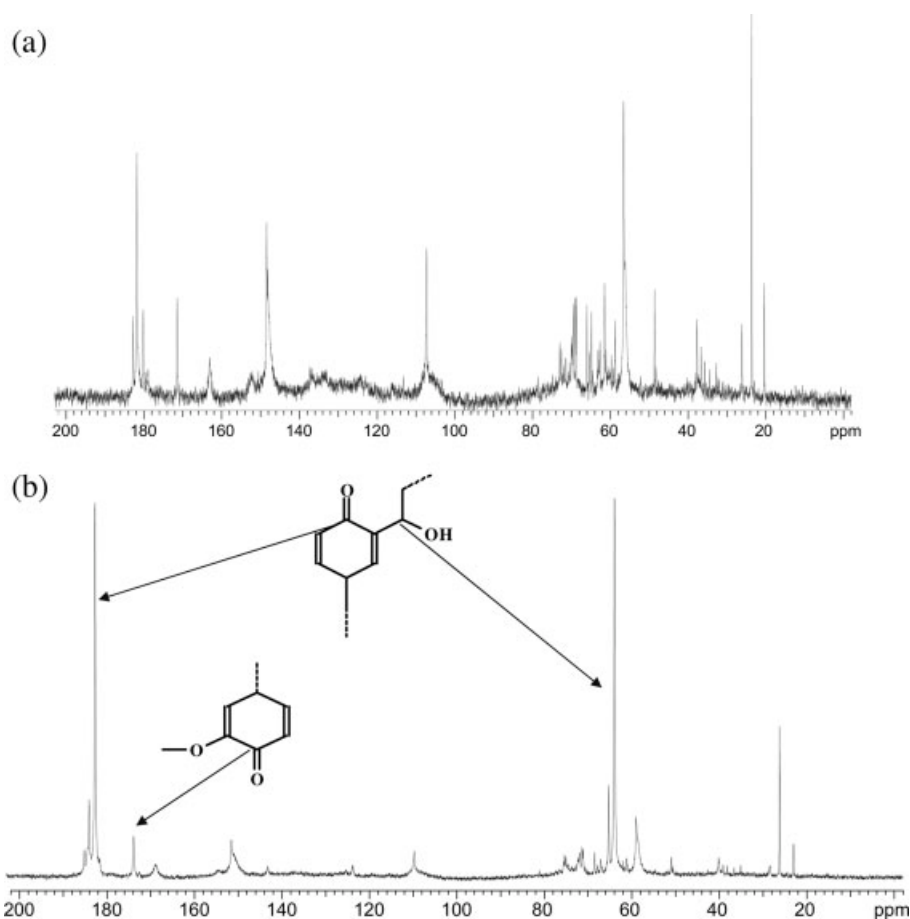


Figure 8 The ¹³C-NMR of (a) original lignin and (b) GLB.

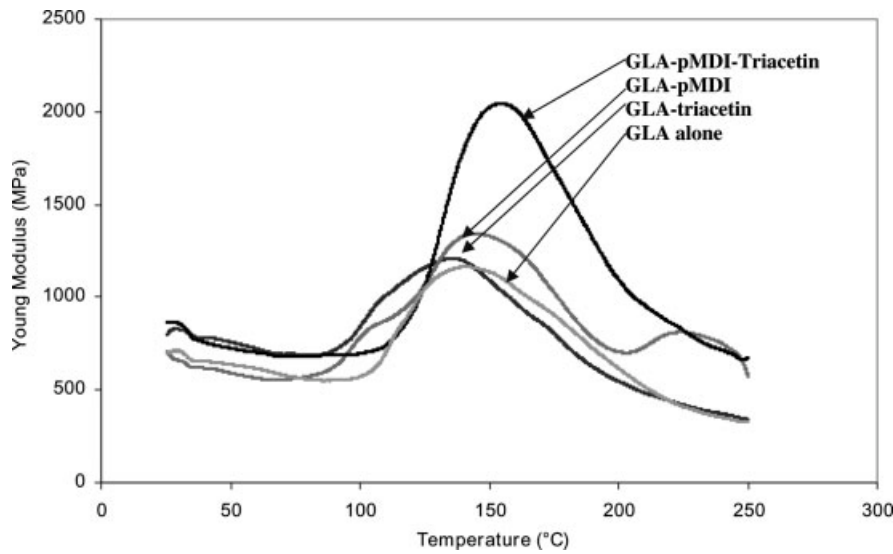


Figure 9 The average curve of the Young's modulus (modulus of elasticity) of a beech joint as a function of the adhesive hardening time obtained by TMA testing (temperature increase rate = 10°C/min) when bonded with GLA, GLA-pMDI (60/40), GLA-pMDI-triacetin (60/40/4% based on solid lignin), and GLA-triacetin (4% based on solid lignin).

and MLB and including different relative proportions of ML, isocyanate, and PF resin, the mix of the three resins being the early concept advanced previously.^{8,9} The results in Table I confirm several findings of the TMA scans and new findings. First, MLB is generally the best performer for the type of lignin used, confirming what is shown by TMA. Second, all formulations give panels satisfying the dry IB strength requirements of international standard specifications for interior particleboard.¹⁸ The IB strength standard after 2-h boiling¹⁸ is satisfied by two for-

mulations, the original 55/20/25 ML/pMDI/PF and, of even more interest, 60/40 ML/pMDI, in which the synthetic PF resin has been eliminated. MLB performs better than MLA as expected. Even more encouraging is that a 75/25 MLB/pMDI formulation without any PF presents an IB strength after boiling that is almost up to the level required by the standard. This indicates the ML/pMDI formulations containing only around 30% pMDI and still satisfying the standard are achievable. In Table I the control panels made with the same quantities of pMDI

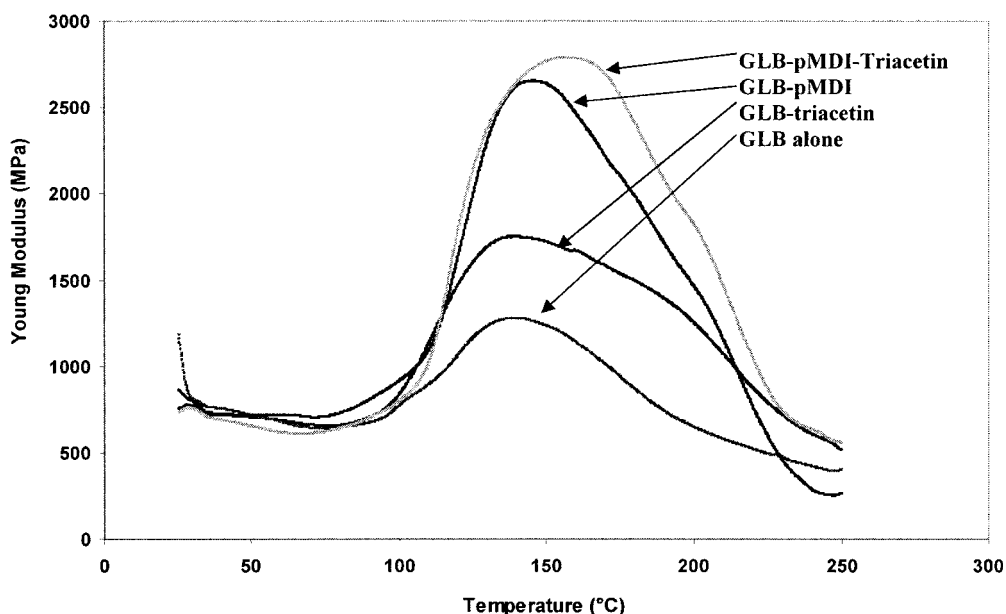


Figure 10 The average curve of the Young's modulus (modulus of elasticity) of a beech joint as a function of the adhesive hardening time obtained by TMA testing (temperature increase rate = 10°C/min) when bonded with GLB, GLB-pMDI (60/40), GLB-pMDI-triacetin (60/40/4% based on solid lignin), and GLB-triacetin (4% based on solid lignin).

TABLE III
Reactant Proportions Used to Prepare Glyoxalated Lignins GLA and GLB

	GLA	GLB
Lignin (g)	29.5	29.5
Glyoxal 40% in water (g)	8.75	17.5
Sodium hydroxide (30%)	14.1	18.1
Water (g)	47.65	38.4

but without any of the other components show that the combination of ML/pMDI gives a greatly improved result than the control and the good IB strength was not due to only the isocyanate.

Table II provides the results of particleboard bonded with the best two lignin-based adhesive systems and prepared at progressively faster pressing times, the pressing time of a board being the most relevant parameter determining the yield. All IB strength values that were obtained, both dry and after a 2-h boil, satisfy the relevant requirements of the standard¹¹ down to press times significant for industrial application.

The ¹³C-NMR spectra of the lignin before methylation or glyoxalation (spectrum a, Fig. 8) and after glyoxalation (spectrum b, Fig. 8) indicate that only a few main peaks have increased, varied, or appeared after glyoxalation. The most important one is the 64-ppm peak that corresponds to the benzyl alcohol type group formed by the reaction of glyoxal with the ortho site of the aromatic ring of a phenolic type lignin, thus of a lignin part without methoxy groups in the ortho site. The aromatic ring on which this benzyl alcohol type group is linked is in the form of a quinone. This is supported not only by the shift of the benzyl alcohol type group formed but also by the marked increased intensity of the 182.6-ppm peak that corresponds to the shift of the aromatic carbon of a quinone to which the carbon of the benzyl alcohol type group is linked. Thus, glyoxal has reacted on the aromatic groups of lignin. The 174-ppm peak due to the quinone methide form of methoxylated guayacyl type lignin is also new. The heating of lignin in air during glyoxalation explains the

increased presence of quinones obtained by oxidation in air of some of the phenolic hydroxy groups of lignin. The spectra of equivalent lignins after methylation are not reported here because we reported them elsewhere in 2006¹⁶ and over a decade ago in 1993.⁸

The results in Figures 2 and 3 indicate the comparative performance of different adhesive formulations when using GL type A (GLA, Fig. 9) and type B (GLB, Fig. 10, Table III). In the case of the lower glyoxalation level (GLA), Figure 9 shows that, although the addition of triacetin mainly accelerates the formation of substituted methylene bridges between lignin aromatic nuclei as indicated by the earlier rise of the MOE curve, the addition of only MDI mainly improves the strength of the joint as exemplified by the higher MOE value. However, it is the combination of both triacetin accelerator and MDI coreactant that considerably improve the final strength of the joint. In the case of the higher glyoxalation level (GLB) in Figure 10, the relation of the different effects is different. Thus, the main differences are that, first, with the GLB formulation higher MOE values are obtained and, second, there is little difference once MDI is added to GLB regardless of whether the triacetin accelerator is added. Its addition still gives the best performance but the difference is slight. It is also noticeable that the addition of triacetin accelerator in the lignin with a higher glyoxalation level yields a larger improvement than that observed for GLA. This would be expected because triacetin ester accelerator is known to participate in the polymer network in PF resins, more with higher levels of methylation.¹⁹⁻²¹

Table IV reports the results of two formulations for lignin adhesives that were optimized for lignin-formaldehyde adhesives and translated and applied to the two types of GL. A long pressing time was used. All formulations gave excellent results, and the IB strength values of the panels satisfied the requirements of international standard specifications for exterior-grade performance.¹⁸ The results of the 60 : 40 formulations were remarkable, as the need for the addition of a PF resin was overcome. How-

TABLE IV
Effects of Component Ratio When Using Glyoxalated Lignin (10% = Adhesive Content) on Particleboard

N	ML/pMDI/PF component ratio	Dry		Boiled (2 hours)	
		Density (g/cm ³)	IB (MPa)	Density (g/cm ³)	IB (MPa)
A	55/20/25	0.697	0.69	0.692	0.15
A	60/40/00	0.714	0.73	0.720	0.20
B	55/20/25	0.716	0.76	0.714	0.20
B	60/40/00	0.706	0.78	0.697	0.19
	EN 312		≥ 0.35		≥ 0.15

Pressing time = 7.5 min, temperatures = 195 – 200°C, thickness = 14 mm.

TABLE V
Effect of Different Components Ratio When Using Glyoxalated Lignin (10% = Adhesive Content)

pMDI	Pressing time (min)	Formaldehyde emission (mg/100 g)	Dry		Boiled for (2h)	
			Density (g/cm ³)	IB (MPa)	Density (g/cm ³)	IB (MPa)
60/40 (10%)	7.5	0.7	0.706	0.81	0.713	0.20
60/40 (10%)	5.5	0.7	0.716	0.73	0.727	0.20
60/40 (10%)	4.5	0.6	0.711	0.71	0.708	0.16
60/40 (10%)	3.5	0.6	0.719	0.67	0.692	0.12
EN 312				≥ 0.35		≥ 0.15

Triacetin 4% on the methylol group forms used lignin or lignin + PP.

ever, because glyoxal is less reactive than formaldehyde, the real proof of the adhesives' suitability for industrial applications is how fast the panel can be pressed and the adhesive cured while still satisfying the relevant standard specification. Table V provides the IB strength results obtained for panels with 60/40 GLB/pMDI tested at pressing times as short as 3.5 min and at 15 s/mm panel thickness at 195°C. These results indicate that the boiled IB strength still satisfies the relevant standard specification at a 4.5-min pressing time and the results are lower but not too far from satisfying the standard at the 3.5-min press time. If it is considered that modern industrial particleboard presses operate at 220°C and the higher the temperature is the shorter the pressing time achieved, the results in Table V indicate that our formulations can be pressed at even faster times than those indicated, well within the range of significant press times, while still complying with the standard requirements.

Of importance in wood panel manufacture is also the percentage of adhesive used because this influences the cost of the panel, as well as the percentage of the more costly pMDI in the formulation. Table VI presents the IB strength values of panels prepared by progressively decreasing the percentage resin load on dry wood from 10 to 6%. The results indicate that the formulation is able to pass the requirements for a fully exterior-grade board down to 8% resin load on dry wood. This corresponds to 3% pMDI in the board, a percentage much lower than

the 5–6% pMDI that would be needed to obtain the same performance by using pMDI alone. Of equal interest is the IB strength results obtained with a 70/30 GLB/pMDI formulation. These are slightly lower than the requirements of the standard, under the conditions used, but they will almost certainly be able to satisfy the standard if pressed industrially at 220°C rather than the 195°C to which the experiment was limited because of the physical limitations of our laboratory presses. This is also a clear supporting indication that even a 70/30 MLB/pMDI formulation will pass all the standard requirements, formaldehyde being much faster reacting than glyoxal.

CONCLUSION

Lignin-based wood adhesives were obtained that satisfy the requirements of relevant international standards for the manufacture of exterior-grade wood particleboard. Formulations based on low molecular mass lignin and presenting an increase in the relative proportion of reactive points yielded better results than the higher molecular mass lignin used in the past. These lignin-based adhesives also produced acceptable results at particleboard pressing times that were sufficiently low to be of industrial significance.

Lignin-based wood adhesives in which formaldehyde was not used in their preparation and which was substituted by a nonvolatile, nontoxic, albeit slower reacting, aldehyde (glyoxal) were prepared

TABLE VI
Effect of Adhesive Content on Particleboard

Adhesive content GLB/pMDI	DRY		Boiled (2 h)	
	Density (g/cm ³)	IB (MPa)	Density (g/cm ³)	IB (MPa)
60/40 (10%), 60/40	0.715	0.77	0.698	0.21
60/40 (9%), 54/36	0.717	0.74	0.684	0.21
60/40 (8%), 48-32	0.708	0.70	0.712	0.17
60/40 (7%), 42/28	0.720	0.60	0.703	0.09
60/40 (6%), 36/24	0.695	0.49	0.721	0.06
70/30 70/30	0.687	0.65	0.692	0.13
EN 312		≥ 0.35		≥ 0.15

Pressing time = 7.5 min. temperature = 195–200°C, thickness = 14 mm.

and tested for application to wood panels such as particleboard. The adhesives not only yielded good IB strength results of the board to pass comfortably relevant international standard specifications but also showed sufficient reactivity to yield panels with press times comparable to that of formaldehyde-based commercial adhesives.

References

1. Nimz, H. In *Wood Adhesives: Chemistry and Technology*; Pizzi, A., Ed.; Marcel Dekker: New York, 1983; Vol. 1.
2. Abe, I. *Mokuzai Kyogo* 1987, 42, 151.
3. Feldman, D. In *Chemical Modification, Properties and Usage of Lignin*; Hu, T. Q., Ed.; Kluwer Academic/Plenum: New York, 2002.
4. Lewis, N. G.; Lantzy, T. R. *Lignin in Adhesives. Introduction and Historical Perspective*; Glasser, W. G.; Sarkanen, S.; Eds.; ACS Symposium Series 397; American Chemical Society: Washington, DC, 1989; p 13.
5. Pecina, H.; Kuchne, G. *Ann Warsaw Agric Univ Forest Wood Technol* 1995, 46, 93.
6. Roffael, E.; Dix, B. *Holz Roh Werkstoff* 1991, 49, 199.
7. Shiraiishi, N. In *Recent Progress in Wood Dissolution and Adhesives from Kraft Lignin*; Glasser, W. G.; Sarkanen, S.; Eds.; ACS Symposium Series 397; American Chemical Society: Washington, DC, 1989; p 488.
8. Stephanou, A.; Pizzi, A. *Holzforschung* 1993, 47, 439.
9. Stephanou, A.; Pizzi, A. *Holzforschung* 1993, 47, 501.
10. Batubenga, D. B.; Pizzi, A.; Stephanou, A.; Cheeseman, P.; Krause, R. *Holzforschung* 1995, 49, 84.
11. Pizzi, A.; Walton, T. *Holzforschung* 1992, 46, 541.
12. Despres, A.; Pizzi, A.; Delmotte, L. *J Appl Polym Sci* 2006, 99, 589.
13. Wieland, S.; Pizzi, A.; Hill, S.; Grigsby, W.; Pichelin, F. *J Appl Polym Sci* 2006, 100, 1624.
14. National Institute for Occupational Safety and Health. *Registry of Toxic Effects of Chemical Substances*; National Institute for Occupational Safety and Health: Washington, DC, 2000.
15. National Technical Information Service. *Publication AD-A125-539*; National Technical Information Service: Washington, DC, 1977.
16. El Mansouri, N.; Salvado, J. *J Appl Polym Sci*, to appear.
17. Pizzi, A.; Lu, X.; Garcia, R. *J Appl Polym Sci* 1999, 71, 915.
18. European Norm EN 312-5. *Particleboard—Exterior Grade*; European Commission: Brussels, Belgium, 2004.
19. Pizzi, A.; Garcia, R.; Wang, S. *J Appl Polym Sci* 1997, 66, 255.
20. Zhao, C.; Pizzi, A.; Garnier, S. *J Appl Polym Sci* 1999, 74, 359.
21. Lei, H.; Pizzi, A.; Despres, A.; Pasch, H.; Du, G. *J Appl Polym Sci* 2006, 100, 3075.