Environment-Friendly Soy Flour-Based Resins Without Formaldehyde

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ABSTRACT: Glyoxalated soy flour adhesives for wood particleboard added with a much smaller proportion of glyoxalated lignin or tannin and without any addition of either formaldehyde or formaldehyde-based resin are shown to yield results satisfying the relevant standard specifications for interior wood boards. Adhesive resin formulations in which the total content of natural material is either 70 or 80% of the total resin solids content gave good results. The resins comprising 70% by weight of natural material can be used in a much lower proportion on wood chips and can afford pressing times fast enough to be significant under industrial panel pressing conditions. The best formulation of all the ones tried was the one based on glyoxalated precooked soy flour (SG), to which a condensed tannin was added in water solution and a polymeric isocyanate (pMDI), where the proportions of the components SG/T/pMDI was 54/16/30 by weight. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 624–632, 2008

Key words: adhesives; soy; tannins; lignin; resins; wood; glyoxal; formaldehyde emission

INTRODUCTION

The great majority of industrial wood products to day are reconstituted materials that are held together by synthetic thermosetting adhesives. The resins used to bind them are in general formaldehyde-based adhesives. Environmental and health considerations have prompted the introduction of more severe standards regarding the emission of formaldehyde from bonded wood products. This, coupled with the increase in costs of oil-derived synthetic resins has intensified the interest in alternative resins based on natural, environment-friendly materials for wood adhesives. Thus, industrially usable formaldehyde-free resins based on condensed tannins,[1–4] on lignin,[5–8] on vegetable oils,[8] and on soy protein and soy flour have been proposed.[9–11]

Although some of these resins are already in industrial use and perform well, i.e., tannin adhesives,[1–3,8] the supply of these latter is still reasonably limited. This renders interest in the use of alternative materials and in coreacting them with other, more abundant and freely available materials, such as soy flour, to extend their use. Soy protein hydrolysates and soy flour are abundant commercial products that have already been used to formulate adhesives

for wood panel products according to two different approaches. First is the prereaction of soy protein or flour with formaldehyde and with synthetic phenol to have soy–phenol–formaldehyde resins either used alone,[10,11] or used in combination with a relatively small proportion of isocyanate (pMDI).[10,11] In these, the natural material is just in the majority (up to 60%). The second approach is through the formation of an adduct of soy protein with maleic anhydride followed by hardening with polyethyleneimmine.[9] Both approaches are good, but the first still suffers of the presence of formaldehyde and the second of the presence of the expensive polyethyleneimmine coupled with a still relatively slow wood board hot press time. Both approaches contain consistently high amounts of synthetic materials: the first of phenol, formaldehyde, and pMDI and the second of maleic anhydride and polyethyleneimmine.

Adhesive resins in which the total content of natural material is much higher than what already achieved, and synthetic materials addition is minimized, would then be of considerable interest. This would be even more interesting if it could be coupled with the total elimination of formaldehyde, while still maintaining good performance at hot pressing times of industrial significance. Glyoxal is a nonvolatile nontoxic aldehyde that has been tested in lignin[5–7] and tannin adhesives[12] for application to wood panels such as particleboard. Glyoxal is a nontoxic aldehyde (LD50 rat ≥ 2960 mg/kg; LD50 mouse

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≥1280 mg/kg),[13] nonvolatile but less reactive than formaldehyde, which is toxic (LD50 rat ≥ 100 mg/kg; LD50 mouse ≥ 42 mg/kg).[14]

This study deals then with the maximization of the natural component of the wood adhesive resins, in absence of formaldehyde, while still satisfying relevant standard requirements for wood board and their adhesives.

EXPERIMENTAL

The soy flour used was a twice precooked and dried commercial soy flour (CELNAT, St.Germain-la-Prade, France). It contained 35.2% proteins, 33.6% carbohydrates, 25.4% lipids, and 7.7% fibers. The lignins used were Protobind 100SA.140, a lower molecular weight (average MW 1500) commercial kraft wood lignin from India sold by Granit , Lausanne, Switzerland, and a lower molecular weight soda bagasse lignin from Brazil. The mimosa tannin extract was spray-dried Ormotan and Tanwat ex SILVA Italy, origin Tanzania, containing 84% phenolic flavonoid material (average MW = 1260), 5% water, and 11% other materials the great majority of which were oligomeric carbohydrates (hydrolysis products of hemicellulose).

Soy flour + formaldehyde[10,11]

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer, and condenser was charged with water (709 g), NaOH (28 g), a phase transfer agent ethylene glycol (5.3 g), and silicon oil (10 drops) and heated to 70°C. Soy flour (350 g) was then charged to the rapidly stirring solution. The mixture was then heated to 90°C over 15 min, with rapid agitation, and held between 88 and 92°C for 1 h. Formaldehyde 37% (134 g) was added to the hot mixture over a 5-min period, less the heat source. The mixture was allowed to stir and maintained between 88 and 92°C for an additional 55 min. The mixture was cooled to 35°C in an ice bath.

Soy flour + formaldehyde + lignin (or phenol)

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and condenser was charged with water (709 g), NaOH (28 g), a phase transfer agent ethylene glycol (5.3 g), and silicon oil (10 drops) and heated to 70°C. Soy flour (350 g) was then charged to the rapidly stirring solution. The mixture was then heated to 90°C over 15 min, with rapid agitation, and held between 88 and 92°C for 1 h. Formaldehyde 37% (134 g) was added to the hot mixture over a 5-min period, less the heat source. The mixture was allowed to stir and maintained between 88 and 92°C for an additional 55 min, followed by the addition of lignin solution (pH = 12 for better dissolution of the lignin powder) (103 g of

TABLE I
Characteristics of Resins Prepared with Precooked Soy Flour by Reaction with Either Formaldehyde or Glyoxal

Resin	Solid content (%)	Viscosity (mPa s)	pH
Soy flour-Glyoxal (SG)	32	1200	4.5
Soy flour-Formaldehyde (SF)	30	880	11.04
Lignin (Brazil)-Glyoxal (LBG)	31	100	13.0
Soy flour-Formaldehyde-Lignin (SFL)	32	440	10.35
Lignin (India)-Glyoxal (LIG)	32	160	12.14

lignin and 150 g of water), while cooling to 75°C over a 10-min period. NaOH (8.8 g) was then added, followed by a second addition of formaldehyde 37% (167.6 g) and two more NaOH charges (4.4 g each). The mixture was held at 75°C for an additional 1.5 h and cooled to 35°C in an ice bath. When an equivalent proportion by weight of phenol was added the formulation used was identical and was derived from the work of other authors.[10,11]

Soy flour + glyoxal

In a three-neck round-bottom flask equipped with a mechanical stirrer, thermometer and condenser was charged with water (709 g), NaOH (28 g), a phase transfer agent ethylene glycol (5.3 g), and silicon oil (10 drops) and heated to 70°C. Soy flour (350 g) was then charged to the rapidly stirring solution. The mixture was then heated to 90°C over 15 min, with rapid agitation, and held between 88 and 92°C for 1 h. Glyoxal (40% in water) (239 g) was added to the hot mixture over a 5-min period, less the heat source. The mixture was allowed to stir and maintained between 88 and 92°C for an additional 2 h and 55 min. The mixture was cooled to 35°C in an ice bath.

The low pH was due to the formation of hydrated sodium salt of glyoxilic acid $(HO)_2CHCOO^-Na^+$ as seen in the RMN spectra. The solid contents, viscosity, and final pH are shown in Table I.

Glyoxalation of lignin

About 29.5 parts by mass of lignin powder (96% solid) (soda bagasse lignin ex Brazil) were slowly added to 47.65 parts water, while sodium hydroxide solution (30%) was added from time to time thus keeping 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 stirrer. A total of 14.1 parts by mass sodium hydroxide solution (30%) was added, which resulted to final pH near to 12.5.

A 250-mL flat-bottom flask equipped with a condenser, thermometer, and magnetic stirrer bar was

charged with the above solution and heated to 58°C. About 8.75 parts by mass glyoxal (40% in water) were added and the lignin solution was then continuously stirred with a magnetic stirrer/hot plate for 8 h. The solid content for all glyoxalated lignin were around 31%.

Blending of glyoxalated soy flour and/or glyoxalated lignin with tannin or PF resins and pMDI

The glyoxalated lignin water solution was thoroughly mixed with either a 45% solution of mimosa tannin extract (ex SILVA Italy, origin Tanzania) at the same pH solution or a synthetic phenol–formaldehyde resin with a solid content around 60% as indicated in the Tables. Only nonemulsified polymeric MDI (pMDI = polymeric 4,4′ diphenyl methane diisocyanate) was used throughout. The diisocyanate raw polymeric MDI (pMDI) was added before application and mixed well according to techniques already reported.[15] In the particleboard preparation, all glue mixtures did have a pH between 11.5 and 12.

Viscosity and resin solids content

Viscosity was done at 25°C with a Brookfield viscometer at the solid contents of application of each resin. The solid contents of each resin is the average of a triplicate gravimetric test, in which specimens of ~ 1 g of each resin were accurately weighed before and after hardening at 105°C for 12 h.

Thermomechanical analysis

The hardening reaction of the glue mixes can be evaluated by TMA by studying the rigidity of a wood-resin joint as a function function of temperature. Thus, different glues mixes as indicated in the figures and tables were analyzed by TMA in bending according to a technique already reported.[15,16] Triplicate samples of two beech wood plys [sliced decorative beech wood (*Fagus sylvatica*) veneers] of 0.6 mm thickness bonded with the test resins as a layer of 350 μm, for a total samples dimension of $21 \times 6 \times 1.2$ mm^3 were tested with a Mettler 40 TMA apparatus (Mettler-Toledo, Giessen, Germany) in three points bending on a span of 18 mm exercising a force cycle of $0.1/0.5N$ on the specimens with each force cycle of 12 s (6 s/6 s). All TMA tests were conducted under the same conditions: heat rate $= 10°C/min$, 30 mg of resin system, temperature range is 25–250°C. The software used for data treatment is STARe. Deflection curves that permit the determination of the modulus of elasticity (MOE) have been obtained by three point bending mode. The classical mechanics relation between force and deflection $Y = [L^3/(4bh^3)][\Delta F/(\Delta f_{wood} - \Delta f_{adhesive})]$ would allow the calculation of the MOE Y for each of the cases tested, although this not the objective of the exercise. As the deflections Δf obtained were proven to be constant and reproducible,[16,17] and they are proportional to the flexibility of the assembly, the relative flexibility as expressed by the MOE of the different adhesive systems can generally be calculated through the relationship $E_1/E_2 = \Delta f_2/\Delta f_1$. This relationship has been used recently to derive a phenomenological equation describing the average number of degrees of freedom of the polymer segments between crosslinking nodes in a hardened polycondensate network on a wood substrate.[16,17] The phenomenological equation was then simplified, by the use of experimental data on all the currently used wood adhesives, to a regression equation of easier applied use. The MOE of a wood-resin system gives a good indication of the end strength of the final application of the glue tested.[18,19] The MOE max-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. Curves in the figures are compared on the basis of the maximum value of the MOE obtained, this indicating the best strength possible in the joint, and on the basis of at which temperature the rise of the MOE starts, indicating the rate of gelling and setting of the resin.

Particleboard manufacture and testing

Duplicate one-layer laboratory particleboard of $350 \times 300 \times 14$ mm^3 dimension were prepared using a mixture of core particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) wood particles at 28 kg/cm^2 maximum pressure and 190–195°C press temperature. The resin solids load on dry wood was maintained at 10% of the total mix of modified soy + isocyanates+ tannin and or lignin when these two were used, except where otherwise indicated in the tables. The total pressing time was maintained at 7.5 min, but a series of boards prepared progressively reducing the pressing times was also done. All particleboard were tested for dry internal bond (IB) strength. The IB strength test is a relevant international standard test[20] done on five board specimens and is a tension test perpendicular to the plane of the board. Thus, each IB and panel density result in the Tables is the average of 10 specimens. The panel density reported in the Tables is the average of the density of the series of specimens for each series of panels.

^{13}C CP-MAS NMR spectra

The soy resin specimens and lignin resin specimens were hardened at 105°C for 2 h in an oven before

being ground finely for NMR analysis. The hardened soy resin, lignin resins and the original lignin, and soy flour were analyzed by solid state CP MAS 13C NMR. Spectra were obtained on a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at sample spin of 4.0 kHz. The impulse duration at 90° was 4.2 ms, contact time was 1 ms, number of transients was about 1000, and the decoupling field was 59.5 kHz. Chemical shifts were determined relative to tetramethyl silane used as control. The spectra were accurate to 1 ppm. The spectra were run with suppression of spinning side bands.

RESULTS AND DISCUSSION

The formulations that evolved from the work reported were first scanned by thermomechanical analysis in bending according to a technique already reported.[18,19] The TMA results are reported in Figures 1–3. The curves of the MOE as a function of increasing temperature for three resins, in which soy flour was reacted with formaldehyde and the soy–formaldehyde adduct reacted with soda bagasse lignin as reported in Figure 1. The formulation and procedure used to prepare these soy–formaldehyde–lignin resins were the same as reported by other authors in the case of soy–formaldehyde–phenol resin[10,11] (soy: phenol by weight = 66 : 34 to 50 : 50). In the resin in Figure 1, the relative proportions of soy flour and formaldehyde were varied from a soy: lignin weight ratio of 77/23 to 56 : 44 and 33 : 67 weight ratios. The results in Figure 1 indicate that (i) substitution of the phenol in the original resin formulation[10,11] with a natural material such as lignin is possible, by this increasing the proportion of natural material in the formulation and (ii) that higher proportion of soy in the resin appeared to give better performance of the bonded joint.
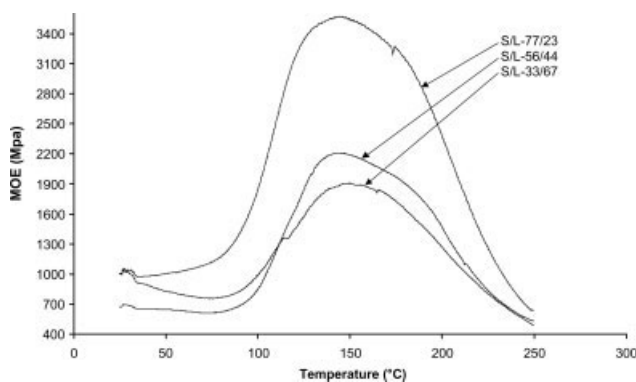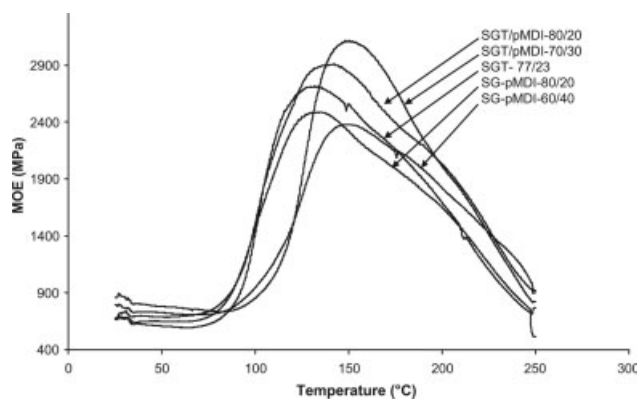

Figure 1 Curves of Young's modulus as a function of temperature obtained by thermomechanical analysis (TMA). The curves are of formaldehyde reacted Soy flour (S) + brasilian soda bagasse lignin (L) coreacted in different proportions by weight.
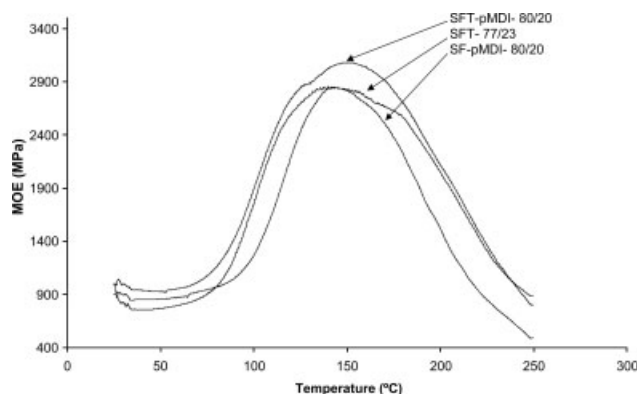
Figure 2 Curves of Young's modulus as a function of temperature obtained by thermomechanical analysis (TMA). The curves are of soy flour reacted with formaldehyde (SF) to which has been added in the glue-mix before application to wood both a water solution of condensed tannin and pMDI. The proportion of natural material to synthetic material are given (SFT/pMDI = 80/20, and SF/pMDI = 80/20), as well as the proportion of SF/tannin when the synthetic resin is absent.

The work of previous authors[10,11] detailing the preparation of soy–formaldehyde–phenol resin envisaged then their reaction *in situ* in the wood board with isocyanate (pMDI, polymeric 4,4' diphenylmethane diisocyanate) to yield industrially significant results. These soy–formaldehyde–phenol–pMDI resins presented relative weight proportions of soy: phenol: pMDI = 60 : 31 : 9, these proportions yielding the best performing resins. However, at first these results could not be reproduced by substituting lignin to phenol in the original formulation (the performance of the original formulation was checked

Figure 3 Curves of Young's modulus as a function of temperature obtained by thermomechanical analysis (TMA). The curves are of soy flour reacted with glyoxal (SG) to which has been added in the glue-mix before application to wood both a water solution of condensed tannin and pMDI. The proportion of natural material to synthetic material are given (for example SGT/pMDI = 80/20), as well as the proportion of SG/tannin when the synthetic resin is absent.

TABLE II
Average Results of Duplicate Laboratory Wood Particleboard Bonded with Different Soy Flour Resins[a]

|	Viscosity (mPa s)	Density (kg/m³)	IB strength (MPa)
Soy flour-Formaldehyde			
Soy flour-Formaldehyde-Lignin Br/pMDI 80-20 (SFLB/p)	440	712 ± 6	0.37 ± 0.02
Soy flour-Formaldehyde/pMDI 80-20 (SF/p)	880	717 ± 5	0.38 ± 0.02
Soy flour-Formaldehyde-Tannin 77-23 (SFT)	1000	713 ± 6	0.23 ± 0.03
Soy flour-Formaldehyde-Tannin77-23/pMDI 80-20 (SFT/p)	1280	718 ± 6	0.41 ± 0.02
Soy flour-Glyoxal			
Soy flour-Glyoxal/pMDI 80-20 (SG/p)	1200	705 ± 5	0.25 ± 0.04
Soy flour-Glyoxal/pMDI 60-40 (SG/p)	1200	712 ± 6	0.72 ± 0.04
Soy flour-Glyoxal-Tannin 77-23 (SGT)	1760	693 ± 6	0.04 ± 0.02
Soy flour-Glyoxal-Tannin 77-23/pMDI 80-20 (SGT/p)	1760	704 ± 6	0.32 ± 0.02
Soy flour-Glyoxal-Tannin 77-23/pMDI 70-30 (SGT/p)	1760	712 ± 6	0.74 ± 0.04

[a] Pressing time 7.5 minutes, thickness 14 mm, press temperature 190–195°C, 10% dry adhesive on dry wood.

and found to be good). For this reason the formulation was altered to take into account resins that were developed by adding just in the glue mix both pMDI and natural condensed tannins to lignin prereacted either with formaldehyde or glyoxal.[5,6] Figure 2 shows the TMA results of soy–formaldehyde–tannin, soy–formaldehyde–pMDI, and soy–formaldehyde–tannin–pMDI resins, in which the relative proportions of soy–tannin extract = 77 : 23 by weight, and of soy + tannin: pMDI = 80 : 20 by weight. All these show that the results that can be obtained can be acceptable. It must be pointed out that differently from the lignin that is prereacted with soy and formaldehyde in the reactor, the tannin is not, as it is just added in the glue-mix as for the pMDI.

The first part of Table II reports the results of laboratory wood particleboard obtained using these adhesives. From these it can be seen that the soy–formaldehyde–tannin resin alone does not satisfy the IB strength results required (≥0.35 MPa). However, soy–lignin–formaldehyde–pMDI (soy:lignin:pMDI = 62 : 18 : 20 by weight), soy–formaldehyde–pMDI (soy:pMDI = 80 : 20 by weight), and soy–formaldehyde–tannin–PMDI (soy:tannin:pMDI = 62 : 18 : 20 by weight) satisfy the relevant requirements of standard specifications for interior type wood particleboard.[21] These results show that boards in which the binder is 80% composed of natural material are possible.

The problem that remains is the presence of the formaldehyde. However, previous studies on the use of a nontoxic, nonvolatile aldehyde, glyoxal, for both tannin and lignin adhesives have shown that glyoxal can well substitute formaldehyde in natural materials for polycondensation resins.[5,6,12] Figure 3 shows the TMA results of formulations in which the reaction product of soy with formaldehyde has been substituted by the reaction resin of soy flour with glyoxal (SG), using the same proportions by weight
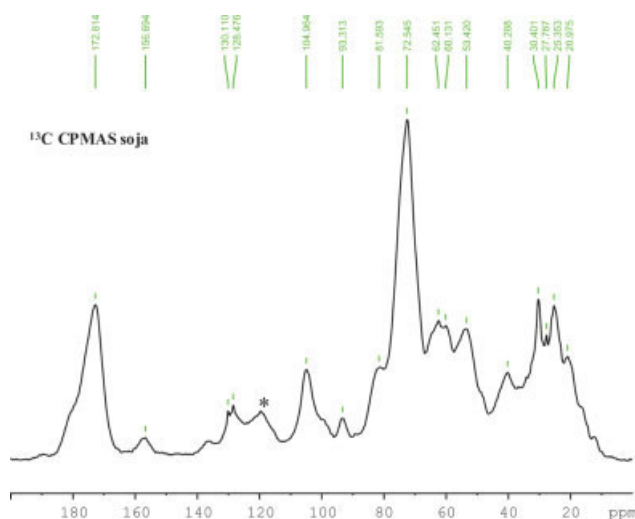
Figure 4 CP-MAS ¹³C NMR of double precooked soy flour. Starting raw material. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
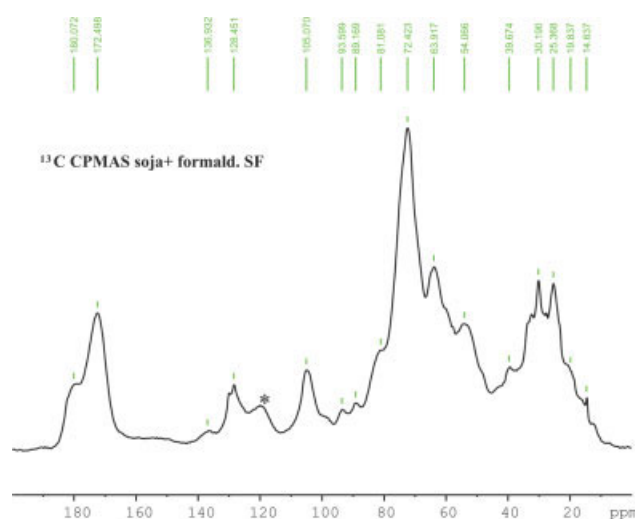
Figure 5 CP-MAS ¹³C NMR of double precooked soy flour reacted with formaldehyde. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
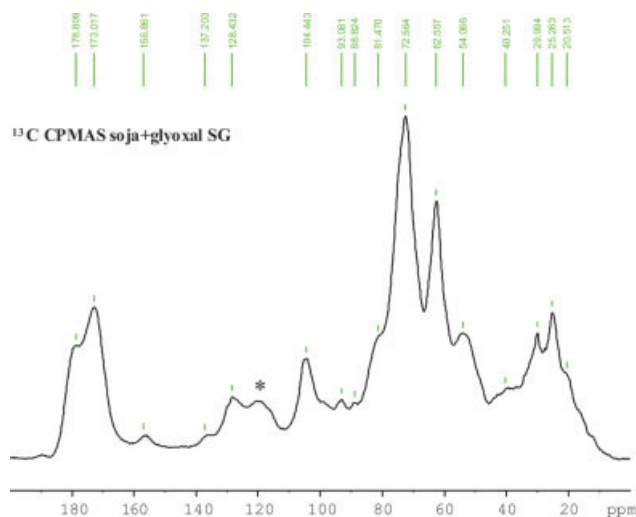
Figure 6 CP-MAS ^{13}C NMR of double precooked soy flour reacted with glyoxal. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of aldehyde and natural material. These show that SG/tannin(T) 77/23, SG/pMDI 80/20, SG/pMDI 60/40 formulations but particularly SG/T/pMDI resins 80/20 and 60/40 (in which SG:T = 77 : 23 by weight) appear to give acceptable results. As the TMA results are only indicative, wood particleboard were also prepared to check the performance of these resins. The results in Table II, second part indicate that the SG/PMDI 60/40 resin is an excellent one, but the high proportion of PMDI renders it possibly too expensive for application, and with a proportion of natural material, which is too low. The SQG/T 77/23 formulation that still appeared reasonable in the TMA gave poor board results. The formulation SG/T/pMDI where SG + T/pMDI is 70/30 and the total proportions by weight are 54/16/30,

for a still rather satisfactory total of 70% natural material and no formaldehyde gives also a very good result. Because of the lower reactivity of glyoxal[12] in relation to formaldehyde, the need to decrease natural material and to increase pMDI was foreseeable.

The reasons for the differences between the SF/T/pMDI and SG/T/pMDI resins can be observed by CP-MAS ^{13}C NMR in Figures 4–6. The spectrum of the double precooked soy flour used for this study with its characteristic peak at 172.8 ppm characteristic of —He C=O of the skeletal peptide link of the protein (—NH—CO—) and the characteristic pattern of the carbohydrates balance present in the flour such as C1 (104.9 ppm), C4 (81.6 ppm), C3, C5 (72.5 ppm), C6 (60–62 ppm), and the CH_3— (20–30 ppm) is reported in Figure 4. Comparing it with Figure 5, where the spectrum of the reaction product of soy with formaldehyde is shown it can be noted that intense band at 63.9 ppm due to the $\rangle N$—CH_2OH group due to the reaction of the amide group of the soy protein with the formaldehyde. There is also the noticeable growth of a band at 33 ppm, this possibly attributed to the formation of formaldehyde-derived methylene bridges linking skeletal amido groups of the protein and/or amino side groups in of certain aminoacids in the protein. Comparing this spectrum (Fig. 5) with the spectrum of glyoxalated soy flour, (Fig. 6) the same intense new peak now shifted to 62.6 ppm and representing here the reactive $\rangle N$—CHR—OH group due to the reaction of the amide group of the soy protein with glyoxal. The peak is even more intense in Figure 6 than in Figure 5 indicating that possibly a greater amount of glyoxal remains reacted in this form than is for formaldehyde. This is supported by the absence in Figure 6 of a band for the —CHR bridge around 33 ppm equivalent to the —N—CH_2—N— bridge band noted for the soy–formaldehyde resin. This is in

TABLE III
Average Results of Duplicate Laboratory Wood Particleboard Bonded with Best Glyoxalated Soy Flour Resin Formulation (SG/T/PMDI = 54/16/30 by weight)[a]

	Viscosity (mPa s)	Density (kg/m^3)	IB strength (MPa)
(i) Resin load series			
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (10%) (SGT/p)	1760	712 ± 6	0.74 ± 0.04
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (9%) (SGT/p)	1760	713 ± 6	0.55 ± 0.04
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (8%) (SGT/p)	1760	712 ± 6	0.56 ± 0.05
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (7%) (SGT/p)	1760	702 ± 6	0.49 ± 0.06
(ii) Pressing time series			
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (7.5 min) (SGT/p)	1760	712 ± 6	0.74 ± 0.04
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (6.5 min) (SGT/p)	1760	702 ± 6	0.77 ± 0.04
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (5.5 min) (SGT/p)	1760	711 ± 6	0.75 ± 0.04
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (4.5 min) (SGT/p)	1760	696 ± 6	0.62 ± 0.06
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (3.5 min) (SGT/p)	1760	688 ± 6	0.50 ± 0.06
Soy flour-Glyoxal-Tanin 77-23/pMDI 70-30 (2.5 min) (SGT/p)	1760	711 ± 6	0.47 ± 0.05

[a] Effect of (i) percentage resin solids content on board dry wood, and (ii) pressing time. Thickness 16 mm, 190–195°C press temperature.

TABLE IV
Average Results of Duplicate Laboratory Wood Particleboard Bonded with Different Mixed Glyoxalated Soy Flour/ Glyoxalated Lignin in Relation to Control Formulations

Mixed soy-glyoxal and lignin-glyoxal	Viscosity (mPa s)	Density (kg/m^3)	IB strength (MPa)
Lignin-Glyoxal/pMDI/PF 55/25/20 (LG/p/PF), control	100	695 ± 6	0.52 ± 0.04
Lignin-Glyoxal/pMDI 60/40 (LG/p), control	100	704 ± 6	0.55 ± 0.04
Lignin-Glyoxal/Tanin/pMDI 55/20/25 (LG/T/p), control	1760	710 ± 5	0.36 ± 0.04
Lignin-Glyoxal-Soy flour-Glyoxal/pMDI 25/50/25 (LBG/SG/p)	1760	702 ± 6	0.48 ± 0.04
Lignin-Glyoxal-Soy flour-Glyoxal/pMDI 25/50/25 (LIG/SG/p)	1760	718 ± 7	0.47 ± 0.04
Lignin-Glyoxal-Soy flour-Glyoxal/pMDI 50/25/25 (LIG/SG/p)	1760	708 ± 6	0.38 ± 0.04

Two different lignins were used: soda bagasse lignin Brazil ex Brazil (LBG) and low molecular weight wood lignin ex India. Pressing time 7.5 min, thickness 14 mm, press temperature 190–195°C.

accord with the lower reactivity of glyoxal in relation to formaldehyde. The greater proportion of these reactive groups present in SG, due to their lack of further transformation into bridges, explains why soy–glyoxal resins do react better than formaldehyde-based ones with either tannin and pMDI, both of these being very reactive with $\rangle N$—CHR—OH groups and $\rangle N$—CH$_2$OH groups.[22–24]

The results in Table III show that the SG/T/pMDI 54/16/30 formulation can be used at lower weight percentages than the 10% used for the results in Tables I and II. Thus, decreasing resin solid contents on dry wood from 10% even down to 7% yield, a considerable decrease, still yields IB strength results satisfying the relevant standard specifications for interior grade boards, and this without any formaldehyde being used. The results of a series, in which boards using the same formulation are pressed at progressively faster pressing times are reported in Table III. Again, pressing times as short as 2.5 min for 16-mm thick panels, hence of 9.4 s/mm panel thickness at 190–195°C press temperature are achieved (Table III), while still satisfying the relevant

international standard specifications for interior grade boards. If it is considered that industrial press temperatures are to day around 220°C, then the pressing time that is derived from this result are industrially significant.

A further, different approach to increase the natural polymer contents of the adhesive formulation was tried, by mixing preglyoxalated lignin with preglyoxalated soy flour (Table IV) in place of either the PF resin or the tannin used in the formulations discussed previously. Two types of lower molecular weight lignins were used, namely soda bagasse lignin ex Brazil and a partially depolymerized wood lignin ex India. Two resin formulations were used: SG/LG/pMDI 50/25/25 and 25/50/25. The other formulations in Table IV are control formulations obtained from other authors.[5,6,10]

The results in Table IV show that all the experimental formulation yield boards satisfying the relevant interior grade standard specifications.[21] They
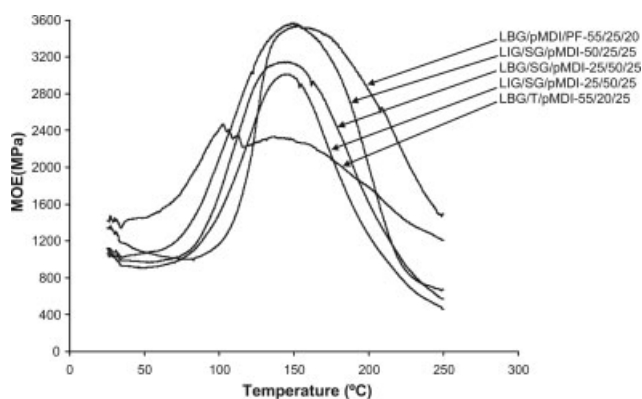
Figure 7 Curves of Young's modulus as a function of temperature obtained by thermomechanical analysis (TMA) of mixed resins baed on glyoxalated soy flour and glyoxalated lignin. Glyoxalated soda bagasse lignin ex Brazil (LBG) and low molecular weight wood lignin ex India (LIG) were used.
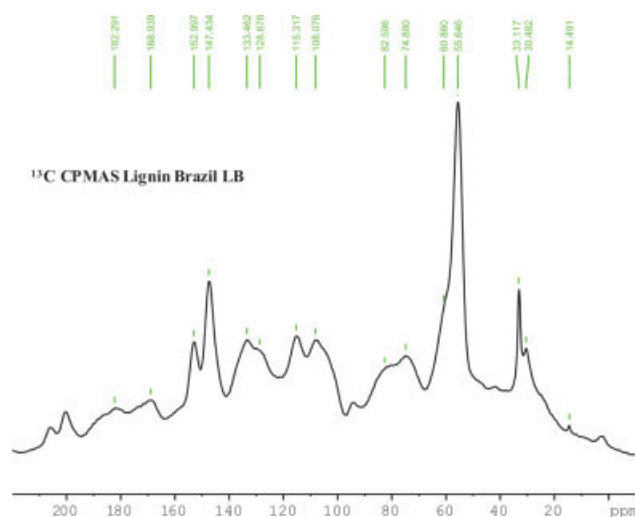
Figure 8 CP-MAS ^{13}C NMR of soda bagasse lignin ex Brazil. Starting raw material. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
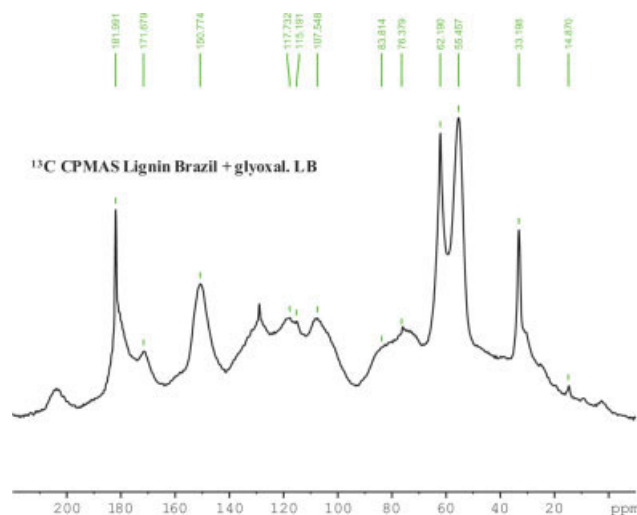
Figure 9 CP-MAS ^{13}C NMR of glyoxalated soda bagasse lignin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

showed too that glyoxalated soy flour gives better results than glyoxalated lignin so that in such mixed SG/LG formulations is better to maximize glyoxalated soy than glyoxalated lignin. Finally, there is no difference in behavior of the two different lignins as regards performance. The thermomechanical results in Figure 7 support the board results shown in Table IV. The CP-MAS ^{13}C NMR spectra of the brazilian soda bagasse lignin before and after glyoxalation are reported in Figures 8 and 9. Comparing the two spectra in Figure 9, different features can be seen with the consequence of the reaction of lignin with glyoxal. The most evident is the appearance of a strong band at 62.2 ppm representing the —CHR—OH group of the benzyl alcohol derived from the first attack of the aldehyde on the aromatic nuclei of lignin. The decrease and disappearance of the 133.5 ppm (Fig. 8) band of one type of meta sites on the crowded aromatic nuclei of lignin indicating that some reaction in meta has occurred on the units, in which all the ortho and para positions are already blocked, such as SG lignins. The disappearance of the two bands at 147.4 and 152.9 ppm accompanied by the growth of the single band of the aromatic nuclei carbon (Ar)C—O— at 150.7 ppm. This can be either due to demethylation of the methoxy groups of SG (Syringyl-Guaiacyl) lignin or to the cleavage of the β-O-4 link between two lignin unit, easily cleaved,[26] and the appearance of a (Ar)C—OH group increasing the reactivity of the ring towards the aromatic ring of the lignin towards the aldehyde. Equally noticeable is the appearance of the sharp intense 181.9 ppm band atributed to HO—CH_2—COO^-Na^+ and the same form attached to lignin namely L–CH_2—COO^-Na^+ due to the known reaction of glyoxal in water.[27,28]

CONCLUSIONS

Glyoxalated soy flour adhesives for wood particleboard added with a much smaller proportion of glyoxalated lignin or tannin and without any addition of either formaldehyde or formaldehyde based resin are shown to yield results satisfying the relevant standard specifications for interior wood boards. Adhesive resin formulations in which the total content of natural material is either 70 or 80% of the total resin solids content gave good results. The resins comprising 70% by weight of natural material can be used in a much lower proportion on wood chips and can afford pressing times fast enough to be significant under industrial panel pressing conditions. The best formulation of all the ones tried was the SG/T/pMDI 54/16/30 by weight.

In relation to previous soy-based adhesives based on reaction with formaldehyde, the resins presented here have several advantages: (i) they cannot present and do not present any aldehyde emission as neither formaldehyde nor any other volatile aldehyde was used and (ii) the percentage of natural materials has been incresed from 55 to 60% in previous formulations to 80% in these new resins. Furthermore, in relation to resin formulations based on different crosslinking reactions[9] other than those with formaldehyde, the resins presented here have other advantages; the pressing times that can be used are much faster and fast enough to be of significance for industrial use in particleboard and other wood chips products. Lastly, they are competitive with alternate natural resin systems such as those based exclusively on tannins and/or lignins, the advantage being that they are able to supplement with a very abundant and inexpensive material, soy flour, materials of excellent performance such as tannins but to day relatively more scarce.

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