

EFFECT OF CHEMICAL MODIFICATION OF LIGNIN ON THE GLUEBOND PERFORMANCE OF LIGNIN-PHENOLIC RESINS

G. Vázquez, J. González, S. Freire & G. Antorrena*

Department of Chemical Engineering, Faculty of Chemistry, University of Santiago de Compostela, 15706 Santiago de Compostela, Spain

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Abstract

Lignin obtained from eucalyptus wood by acetic acid pulping was methylolated or phenolated and used to prepare lignin-phenol-formaldehyde resins. The amount of formaldehyde consumed in the methylolation reaction, and supporting comparison of pre- and post-methylolation ^1H and ^{13}C NMR spectra, showed the reactivity of the crude acetosolv lignin with formaldehyde to be relatively high. Pine and eucalyptus plywood boards manufactured using the resins prepared with the modified lignins complied with European Standard EN 314-1:1993 for WBP quality boards and gave knife test results similar to those of boards manufactured with a commercial phenol-formaldehyde resin. © 1997 Elsevier Science Ltd.

Key words: *Eucalyptus globulus* wood, acetic acid pulping, acetosolv lignin, methylolation, phenolation, lignin-phenol-formaldehyde resin, plywood.

INTRODUCTION

As one of the structural components of plants, lignin is one of the most abundant of renewable natural products. It is made up of phenylpropane units whose substituents and linkages depend on the plant species, although the composition of lignin obtained as a by-product of the wood pulping industry depends not only on the wood pulped but also on the pulping process and the procedure used to isolate the lignin from the pulping liquor (Glasser, 1981; Vázquez *et al.*, 1997). Lignins of particularly high purity can be obtained by organosolv pulping processes.

Because of the ready availability of lignin, and the high cost and toxicity of phenol, the similarity between the structure of lignin and that of phenol-formaldehyde (PF) resins has prompted research on its use as a substitute for phenol in these resins. Crude lignin can react with formaldehyde and other

cross-linking agents at unsubstituted aromatic positions and other active sites, but its capacity for condensing with itself and with PF resins is nevertheless limited, allowing only about 20% of the phenol in a PF resin to be replaced by crude lignin (Hse and Hong, 1989; Vázquez *et al.*, 1995). Higher percentages can be achieved only if the reactivity of the lignin is chemically enhanced, the most promising reactivity-enhancing processes being methylolation (Barry *et al.*, 1993; Oh *et al.*, 1994; Sellers *et al.*, 1994; Olivares *et al.*, 1995), phenolation (Ysbrandy *et al.*, 1992) and demethylation (Chen, 1995). For example, reaction of lignin with formaldehyde in an alkaline medium introduces methylol groups (which can condense with other lignin molecules or phenol-formaldehyde pre-polymers) at position C5 of guaiacyl units (the Lederer-Manasse reaction), at sidechain positions α to a carbonyl group (the Tollens reaction) and on the β carbon of α - β double bonds conjugated to free phenol units (the Prins reaction) (Campbell and Walsh, 1985).

Lignins obtained as co-products by organosolv pulping (organosolv lignins) have properties making them particularly attractive for use in adhesives, including high hydrophobicities, low glass transition temperatures, low polydispersity as regards molecular weight and high functionalization (Senyo *et al.*, 1996). Following reactivity enhancement, they have been successfully used as partial substitutes for phenol in PF resins.

In previous work (Vázquez *et al.*, 1995), we found that when more than 20% of the phenol in a PF resin was replaced by unmodified eucalyptus/acetosolv lignin the lignin acted as a filler and reduced the resistance of plywoods manufactured with the resulting adhesive. We now report the characteristics of resins prepared by co-polymerization of phenol and formaldehyde with methylolated or phenolated eucalyptus/acetosolv lignin, and the gluebond performance of these resins when employed to manufacture exterior grade pine and eucalyptus plywood boards.

*Author to whom correspondence should be addressed.

METHODS

Obtention of lignin

Eucalyptus/acetosolv lignin was obtained by pulping *Eucalyptus globulus* chips for 2 h with an 80% (w/w) aqueous solution of acetic acid, either at 180°C and without mineral acid catalyst (lignin L1) or at 160°C in the presence of a concentration of 0.025% (w/w) of hydrochloric acid (lignin L2); the solid/liquid ratio was in both cases 1/10. Pulping was carried out with mechanical stirring in a 17 l stainless steel (Hastelloy C276) reactor thermostatted by means of a temperature sensor and an internal cooling coil. Wood chips, glacial acetic acid and water were mixed at room temperature and heated, and for lignin L2 HCl was added when the mixture was near its boiling point. The 2 h reaction time was deemed to start when the desired temperature was reached, which occurred after about 2.6 h for L1 and 2.3 h for L2. When the 2 h reaction time had elapsed, the mixture was cooled and the pulp was filtered out of the mother liquor, washed with acetic acid solution and abundant water, and stored in the cold; both the yield and lignin content of the pulp were determined, the latter as the sum of Klason lignin (T222m-54) and acid-soluble lignin (Maekawa *et al.*, 1989).

The mother liquor was pooled with the acetic acid used to wash the pulp, this mixture was concentrated by vacuum distillation at 55–60°C, and the resulting concentrate was diluted with about seven volumes of water in order to precipitate lignin, which was isolated by centrifugal filtration, washed with abundant water and air dried. The purity of this lignin was evaluated by determining (a) its acid-insoluble fraction, by two-step acid hydrolysis (first step, 2 h with 72% H₂SO₄ at room temperature in the ratio 1 g of lignin to 15 ml of acid; second step, 1 h with 3% H₂SO₄ at 120°C); and (b) its reducing sugar content, by the Somogyi–Nelson method.

Methylation of lignin

For characterization of the methylation process, lignin L1 was methylated by reaction for 4 h at 50°C with formaldehyde [formaldehyde/lignin ratio 0.36 (w/w)] in the presence of soda [soda/lignin ratio 0.3 (w/w)]; the solids content of the reaction mixture was 21.5%. The lignin was slowly added, with stirring and at room temperature, to an appropriate mixture of soda and water, and when the lignin had completely dissolved the mixture was heated to 50°C, the formaldehyde was added and the reaction time was deemed to start. The concentration of formaldehyde in samples taken periodically from the reaction mixture was determined by the hydroxylamine hydrochloride method (Walker, 1964; Wooten *et al.*, 1988; Wooten *et al.*, 1990). After 4 h, the reaction mixture was brought to pH 4 by addition of 0.5 N sulphuric acid, and the lignin thus precipitated was separated by centrifugation, washed twice with

distilled water and air dried prior to characterization by NMR spectroscopy (Kuo *et al.*, 1991).

Methylated L1 for preparation of lignin–phenol–formaldehyde resins was obtained in the same way except that, in order to keep the solids content of the final resins about 40%, that of the methylation reaction mixture was raised to 30% (higher values were not possible because of the limited solubility of the lignin). The quantity of formaldehyde that reacted with the lignin was determined by analysis of the final reaction mixture; both unreacted formaldehyde and the soda used in the methylation reaction were taken into account in the subsequent formulation of resins.

Phenolation of lignin

Lignin L2 was phenolated by reaction for 1.5 h at 125°C with phenol [phenol/lignin ratio 2/1 (w/w)] in an acid medium [H₂SO₄/phenol ratio 1/20 (w/w)]; the use of a smaller phenol/lignin ratio was prevented by the poor solubility of the lignin in phenol. The phenol was heated to 50°C, the lignin was added slowly, with continuous stirring, until totally dissolved, the required quantity of H₂SO₄ was added, and the mixture was heated to 125°C, maintained at this temperature for 1.5 h, cooled and stored at 4°C pending use.

NMR spectroscopy

Calculation of the degree of methylation of L1 from the amount of formaldehyde consumed in the methylation reaction is in principle unreliable because, under the alkaline conditions used, formaldehyde can react with itself (the Cannizzaro reaction). An independent estimate of the degree of methylation of L1 was therefore obtained by comparison of pre- and post-methylation ¹H and ¹³C NMR spectra recorded following acetylation of the corresponding lignin form.

Acetylation of lignin

Lignin L1 and methylated lignin L1 (2 g) were both treated at room temperature for 48 h with a 1:1 mixture of pyridine and acetic anhydride (30 ml) [Thring *et al.*, 1991], the reaction mixture was poured into 10 times its volume of ice-cold 1% HCl, and the solid product was filtered off with a Büchner funnel, washed with water until the filtrate was of neutral pH, and dried at room temperature (Glasser and Jain, 1993).

NMR spectra

¹³C (75 MHz) and ¹H (300 MHz) NMR spectra of crude and methylated L1 were recorded on a Bruker AMX300 apparatus. For the ¹H spectra, 10 mg of acetylated lignin was dissolved in 0.5 ml of CDCl₃ containing TMS as internal standard; the numbers of phenolic acetate and aliphatic acetate protons were determined, relative to the number of methoxyl protons, by integration of the correspond-

ing signals. For the ^{13}C spectra (recorded without nOe), 200 mg of acetylated lignin was dissolved in 0.5 ml of DMSO- d_6 ; the spectra of the methylolated and unmethylolated lignins were compared in terms of signal heights relative to those of the methoxyl groups.

Preparation of resins

Methylolated lignin-phenol-formaldehyde (MLPF) resins

To enable statistical analysis of the dependence of resin properties and board quality (Y_j) on the percentage of substitution of phenol by methylolated lignin (%S), the formaldehyde/phenol mole ratio (F/P) and the soda/phenol mole ratio (S/P), a 2^3 factorial design was used with %S = 20 or 40%, F/P = 1.8 or 2.2, and S/P = 0.5 or 0.7 (Table 1, MLPF1-8). In addition, two resins (MLPF9 and MLPF10) were prepared independently of each other with %S, F/P and S/P values (30, 2.0 and 0.6, respectively) corresponding to the central point of the 2^3 factorial design.

Multiple regression analysis was used to fit the experimental data with polynomials of the form

$$Y_j = b_{0j} + b_{1j}X_1 + b_{2j}X_2 + b_{3j}X_3 + b_{12j}X_1X_2 + b_{13j}X_1X_3 + b_{23j}X_2X_3 + b_{123j}X_1X_2X_3 \quad (1)$$

where X_1 , X_2 and X_3 are normalized variables corresponding to %S, F/P and S/P, respectively.

Phenolated lignin-phenol-formaldehyde (PLPF) resin

The sole lignin-phenol-formaldehyde resin prepared with phenolated lignin was obtained using a formaldehyde/phenol mole ratio F/P = 2, a soda/phenol mole ratio S/P = 0.7, and a substitution level %S = 33% (w/w).

Polymerization

Polymerization was performed at 80°C in a 2 l glass reactor with a temperature controller and Teflon paddle stirrer, condenser, bottom outlet for sampling, and heating jacket. The reaction was halted when viscosity (measured every 15 min at 25°C in a

Brookfield viscosimeter) reached values in the range 400–600 mPa.s. The resin was then cooled and stored at 4°C. Its viscosity, pH, non-volatile solids content, % free phenol (ASTM D 1313-56), % free formaldehyde (determined by the hydroxylamine hydrochloric method) and gel time (measured by ISO 9396 Method B in a Techne GT-3 gelation timer) were determined before its use for preparation of plywood adhesive.

Plywood adhesives were prepared by supplementing the resin with AP303 filler (10 g/100 g of resin) as viscosity modifier.

Plywood manufacture and testing

Square (25 × 25 cm) five-ply boards were manufactured with *Pinus pinaster* and *Eucalyptus globulus* plies with a humidity of 7–8%. Ply thickness was 1.5 mm for pine plies and 1.2 mm for eucalyptus plies. Adhesive was applied at a rate of 300 g/m² for a double glue line. In all cases, 5 min cold pre-pressing was followed by 7 min under 12 kg/cm² at 135°C. Board quality was tested in accordance with the European Standard EN 314-1:1993 and the British Standard BS 6566:Part 8:1985 (knife test) after 12 h steam treatment at a pressure of 2 kg/cm². Duplicate boards were prepared for each of the resins prepared and for a commercial PF resin (P301).

RESULTS AND DISCUSSION

Delignification and lignin composition

The process by which lignins L1 and L2 were obtained afforded pulp yields of 49.6 and 47.1%, respectively. The total lignin contents of these pulps were, respectively, 3.9% (3.5% Klason lignin plus 0.4% acid-soluble lignin) and 4.3% (3.9% Klason lignin plus 0.4% acid-soluble lignin). Since the lignin content of eucalyptus wood is 22.7% (16.6% Klason lignin plus 6.1% acid-soluble lignin), the L1 pulping process achieved 91.5% delignification and the L2 process 91.1%.

Lignins L1 and L2 had acid-insoluble contents of 89.2 and 87.7%, respectively, and reducing sugar

Table 1. Resin formulations used and resin properties

Resin	%S	F/P	S/P	pH	$\mu_{25^\circ\text{C}}$ (mPa.s)	Non-volatile solids (%)	t_{gel} (min)	Free P (%)	Free F (%)
MLPF1	20	1.8	0.5	10.90	1100	39.1	18.6	2.60	0.16
MLPF2 ^a	40	1.8	0.5	9.98	300	38.4	27.4	4.32	0.29
MLPF3	20	2.2	0.5	11.02	407	37.8	14.9	1.47	0.44
MLPF4	40	2.2	0.5	10.02	507	37.5	24.5	3.20	0.48
MLPF5	20	1.8	0.7	11.95	590	40.3	11.1	1.43	0.09
MLPF6	40	1.8	0.7	10.94	390	37.9	24.2	2.30	0.16
MLPF7	20	2.2	0.7	11.70	425	40.7	11.0	1.19	0.14
MLPF8	40	2.2	0.7	10.78	543	38.2	19.4	1.60	0.27
MLPF9	30	2.0	0.6	10.95	720	39.5	17.1	2.72	0.27
MLPF10	30	2.0	0.6	10.88	494	40.5	18.9	2.68	0.28
PLPF	33	2.0	0.7	11.14	417	41.7	18.1	2.89	0.12

^a Separates into two phases unless vigorously stirred.

contents of 1.4 and 1.97%, respectively, the remainder being in both cases acid-soluble lignin.

Methylation

Figure 1 shows the time dependence of the proportion of formaldehyde consumed when L1 was methylolated using a solids content of 21.5%. The data are satisfactorily fitted by the equation

$$x_{\text{CH}_2\text{O}} = -0.3e^{-0.479t} - 0.13e^{-4.014t} + 0.43 \quad (r^2 = 0.9999) \quad (2)$$

which implies a maximum possible conversion rate of 0.43 (0.52 moles per 100 g of lignin) under the reaction conditions employed. With a 30% solids content, the amount of formaldehyde consumed after 4 h reaction was 0.54 moles per 100 g of lignin. According to Sellers *et al.* (1994), these are relatively high conversion rates (>0.5 moles of CH₂O per 100 g of lignin), and as such indicate that the methylolated lignin should co-polymerize with PF resin instead of acting merely as a filler when added to the polymerization reaction mixture.

NMR spectra

Figure 2 shows the ¹H NMR spectra of acetylated methylolated and unmethylolated L1, and Table 2 lists the integrals of the signals near 3.9, 2.3 and 2.0 ppm, which correspond to methoxyl, phenolic

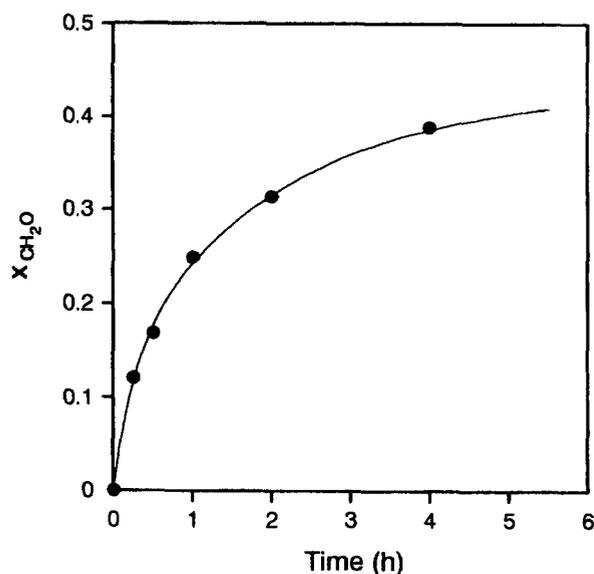


Fig. 1. Quantitative determination of formaldehyde consumption in the reaction of L1 eucalyptus/acetosolv lignin with formaldehyde.

acetate and aliphatic acetate groups, respectively, together with values normalized with respect to the methoxyl signal. The difference of only 0.11 between the normalized values of the aliphatic acetate signals of the methylolated and unmethylolated lignins shows that relatively few methylol groups were introduced by the methylation reaction, a result that may be attributed to L1 having few free C5 positions in its guaiacyl units.

In the ¹³C NMR spectra of L1 (Fig. 3), the introduction of methylol groups at guaiacyl C5 positions is shown by the behaviour of the signals at 142 and 127.7 ppm (Kuo *et al.*, 1991) whose intensities, relative to that of the methoxyl signal, increase from 0.14 to 0.30 and from 0.14 to 0.17, respectively. The

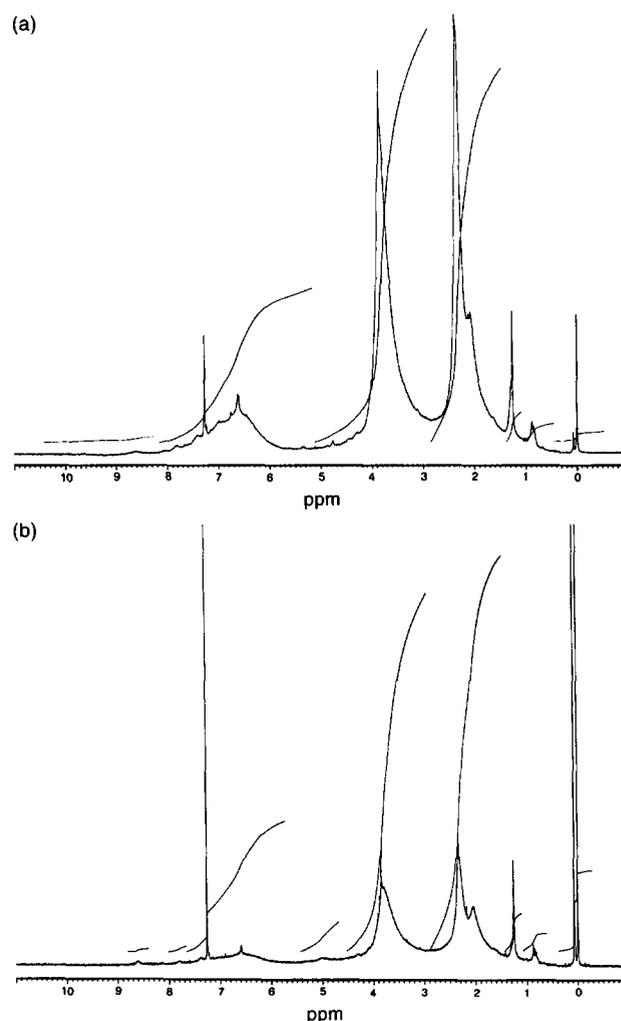


Fig. 2. ¹H NMR spectra of (a) unmethylolated and (b) methylolated eucalyptus/acetosolv lignin.

Table 2. Integrals of various ¹H NMR signals in the acetylated lignin (AL) and acetylated methylolated lignin (AML). Values in parentheses are normalized relative to the integral of the -OCH₃ signal

	-OCH ₃ 4.4–3.2 ppm	φ-Acetate 2.90–2.18 ppm	R-Acetate 2.18–1.40 ppm
AL	17.0 (1.0)	11.1 (0.65)	6.7 (0.39)
AML	15.8 (1.0)	10.4 (0.66)	7.9 (0.50)

increase from 0.14 to 0.19 in the relative intensity of the signal at 60 ppm indicates either the formation of $-\text{CH}_2\text{OH}$ groups on the aromatic ring, or the formation of $-\text{CH}_2\text{-O-CH}_2-$ bridges (Pizzi, 1994).

Resins

All the resins prepared were apparently homogeneous except MLPF2, which separated into two phases and required vigorous stirring before use for plywood board manufacture. All were tacky at room temperature. Their properties are listed in Table 1.

The gel time of the resin prepared from phenolated lignin, PLPF, was about the same as that of

the commercial resin used in the subsequent bonding experiments, 18 min. Those of the MLPF resins ranged from 11.0 to 27.4 min. The only variables with a statistically significant influence on the gel time of the MLPF resins at the 95% significance level were %S and the S/P ratio, in that order (Table 3); Fig. 4(a) shows that for an F/P ratio of 2.0 gel time increased considerably upon increasing the phenol replacement level from 20 to 40%, and fell somewhat upon increasing the S/P ratio. In general, the gel times of the MLPF resins were considerably shorter than those of LPF resins prepared from crude (unmethylolated) eucalyptus/acetosolv lignin (Vázquez *et al.*, 1995), which shows that methylolation of the lignin increased the reactivity of the resin prepared from it.

At the 95% confidence level, the only variables with statistically significant influences on the amount of free phenol in the MLPF resins were again %S and the S/P ratio, although this time the greater effect was that of S/P over the ranges of these variables explored in this work; % free phenol increased with %S and decreased with increasing S/P [Table 3 and Fig. 4(b)]. The amount of free formaldehyde in the MLPF resins was significantly influenced by S/P, F/P, %S and the S/P \times F/P cross-term, in decreasing order of importance (Table 3). For an F/P ratio of 2.0, Fig. 4(c) shows how % free formaldehyde falls with increasing S/P and rises with %S.

Plywood properties

Table 4 lists the knife test results of pine and eucalyptus plywood boards manufactured with the resins prepared in this study, with the commercial PF resin P301, or with mixtures of P301 and PLPF, the LPF resin prepared from phenolated lignin. %S, S/P and F/P had no statistically significant influence on the results of MLPF boards, but eucalyptus board quality did appear to increase slightly with %S, probably because of improved spreading of the adhesive (it is well known — see, e.g. Yazaki *et al.* (1993) — that the high extract content of eucalyptus leads to poor wettability and has negative effects on the gelling and rheology of resins); improved spreading also, of course, implies more economical use of

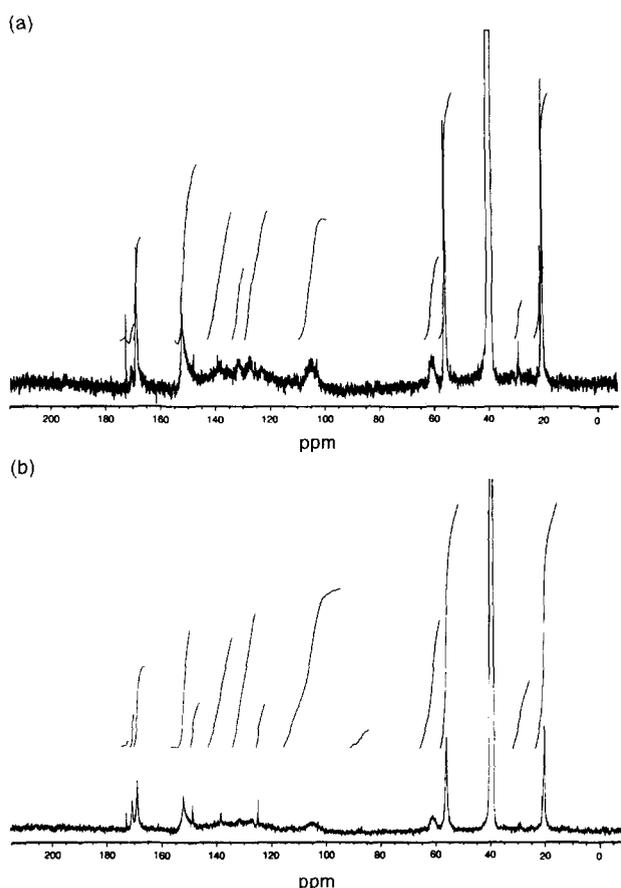


Fig. 3. ^{13}C NMR spectra of (a) unmethylolated and (b) methylolated eucalyptus/acetosolv lignin.

Table 3. Coefficients of the model [eqn (1)] for Y_1 (gel time), Y_2 (% free phenol) and Y_3 (% free formaldehyde) and the statistical parameters establishing their validity

	Y_1	Y_2	Y_3
b_{0j}	18.71	2.35	0.257
b_{1j}	4.98	0.59	0.046
b_{2j}	-1.44 NS	-0.40 NS	0.079
b_{3j}	-2.46	-0.63	-0.089
b_{12j}	-0.49 NS	-0.06 NS	-0.004 NS
b_{13j}	0.39 NS	-0.27 NS	0.004 NS
b_{23j}	0.21 NS	0.16 NS	-0.039
b_{123j}	-0.69 NS	-0.06 NS	0.019 NS
R^2	0.9895	0.9639	0.9971
F-ratio	26.91	7.64	97.91
Prob $F_{\text{exp}} > F_{\text{tab}}$	0.002	0.090	0.000

NS = Non-significant at the 95% confidence level.

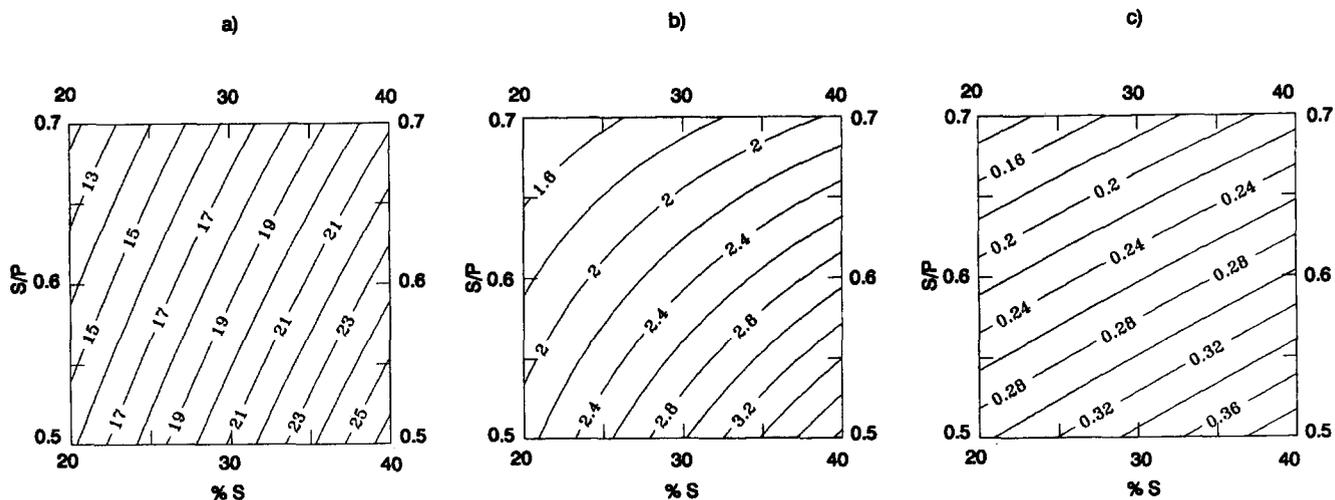


Fig. 4. Dependence of gel time (a), % free phenol (b) and % free formaldehyde (c) on the percentage of substitution of phenol by methylolated lignin (%S) and soda/phenol mole ratio (S/P) at a formaldehyde/phenol mole ratio (F/P) of 2.0.

adhesive. Board quality also seemed to increase somewhat with F/P and S/P, at least when the phenol replacement level was 40%. Apart from these observations, differences among the results for different boards of the same wood, and between the two results for a single kind of board, may be attributed not only to the subjectivity of the test, but also to variation in the rotary-peeled veneers used as plies.

All the pine boards except those manufactured with MLPF4 and MLPF9 had knife test results similar to those of the P301 board and met the standard for WBP quality boards (and the results for the MLPF9 boards are of questionable representativity because, in view of the composition of MLPF9, they would be expected to lie somewhere in the middle of the result range, like those of the boards made with MLPF10, which has the same composition as

Table 4. BS 6566:Part 8:1985 knife test ratings for pine and eucalyptus plywood boards manufactured with methylolated or phenolated lignin-phenol-formaldehyde resins

Resin	Pine plywoods		Eucalyptus plywoods	
	Glue lines	Mean	Glue lines	Mean
MLPF1	5-4-5-5	4.8	4-4-5-4	4.3
	6-5-5-4	4.8	—	—
MLPF2 ^a	4-4-5-4	4.3	5-4-4-6	4.8
	5-4-3-5	4.3	3-4-4-5	4.0
MLPF3	5-5-4-5	4.8	3-4-3-4	3.5
	4-5-6-4	4.8	5-6-5-4	5.0
MLPF4	3-3-4-5	3.8	5-5-4-5	4.8
	4-3-3-4	3.5	5-3-3-4	3.8
MLPF5	5-5-4-6	5.0	—	—
	4-6-5-4	4.8	3-4-4-6	4.3
MLPF6	5-5-5-5	5.0	5-5-4-5	4.8
	5-4-6-5	5.0	6-5-4-4	4.8
MLPF7	6-5-5-6	5.5	3-4-4-6	4.3
	5-5-5-6	5.3	3-5-5-4	4.3
MLPF8	5-6-4-5	5.0	8-5-6-5	6.0
	6-5-4-7	5.5	6-4-5-4	4.8
MLPF9	2-3-4-4	3.3	2-3-3-2	2.5
	4-4-4-3	3.8	2-3-4-2	2.8
MLPF10	5-6-5-5	5.3	4-4-5-6	4.8
	4-6-5-5	5.0	3-5-4-6	4.5
P301	5-5-5-5	5.0	—	—
	6-4-5-5	5.0	4-4-4-5	4.3
PLPF	3-4-5-6	4.5	4-5-4-5	4.5
	2-5-5-4	4.0	5-4-5-4	4.5
50%P301	7-7-6-7	6.8	5-6-5-6	5.5
50%PLPF				
25%P301	8-7-7-7	7.3	5-5-5-7	5.5
75%PLPF				

^a Separates into two phases unless vigorously stirred.

MLPF9). The same pattern is shown by the knife test results for the eucalyptus boards, except that (a) more boards performed better than the P301 board than in the case of pine boards, and (b) the only boards to meet the standard for WBP boards were those manufactured with MLPF3, MLPF8 and the PLPF/P301 mixtures. In keeping with this, almost all the eucalyptus boards performed worse than the pine boards made with the same resin.

Blowouts (the destructive expansion of trapped vapour when pressure is removed from the board) occurred during the manufacture of eucalyptus boards with P301, MLPF1 and MLPF5. Blowouts are favoured by the low solids contents of these resins, by the relatively high moisture contents of the veneers used, and by the low wettability of eucalyptus. The fact that the resins with higher %S values performed better in this respect is in keeping with Chen's (1995) conclusion that lignin reduces resin run-off by promoting dry-out in the glue line.

Although PLPF boards failed to meet the standard for WBP boards, boards made with 50:50 or 75:25 PLPF/P301 mixtures had much better knife test results than either PLPF or P301 boards, meeting the WBP standard for both pine boards (with results well above the minimum required) and eucalyptus boards (which are notoriously difficult to bond satisfactorily). This synergy may be attributed to the mixtures having better rheology, and spreading better on pine and eucalyptus, than P301, and to their having higher solids contents than PLPF.

Table 5 lists shear strength and percentage wood failure results obtained in accordance with European Standard EN 314-1:1993. The fact that the values of both parameters exhibit much greater dispersion than the knife test results is attributable largely to EN 314-1 testing both gluebond and veneer quality; in this work, in which veneers available at the collaborating industrial plant were used, no attempt

was made to select veneers of uniform quality for board manufacture, and the introduction of this uncontrolled variable prevents statistical analysis of the results for the MLPF boards. The fact that the shear strength values for eucalyptus boards are higher than those for pine boards may similarly be attributed to the effect of veneer quality rather than to any influence of wood type on bonding. However, even though interpretation of the results of Table 5 is hindered by the effect of veneer quality, these results seem to exhibit a certain parallelism with the knife test results of Table 4. All the boards manufactured in this work met the EN 314-1 standard for WBP boards.

CONCLUSIONS

Lignin obtained by acetosolv pulping of *Eucalyptus globulus* wood in the conditions described under Methods had a relatively high reactivity with formaldehyde, as was suggested by the formaldehyde consumption data for the methylation reaction and confirmed by comparison of pre- and post-methylation ¹³C NMR spectra, the increase in the relative intensities of the signals at 142 and 127.7 ppm being a sign of the introduction of methylol groups at guaiacyl C5 positions.

LPF resins obtained by co-polymerization of methylolated eucalyptus/acetosolv lignin with phenol and formaldehyde at phenol replacement levels of 20–40%, soda/phenol mole ratios of 0.5–0.7 and formaldehyde/phenol mole ratios of 1.8–2.2 had gel times of 11.0–27.4 min, which are similar to those of commercial phenol-formaldehyde resins. These gel times are considerably less than those of LPF resins prepared in a previous study using unmodified eucalyptus/acetosolv lignin obtained under the same conditions as in this work, which shows that methy-

Table 5. EN304-1:1993 test results for pine and eucalyptus plywood boards manufactured with methylolated or phenolated lignin-phenol-formaldehyde resins

Resin	f_v (N/mm ²)	Pine plywoods		Eucalyptus plywoods	
		f_v (N/mm ²)	Wood failure (%)	f_v (N/mm ²)	Wood failure (%)
MLPF1	1.57		90	5.33	20
MLPF2 ^a	2.27		40	4.00	45
MLPF3	2.28		50	5.10	25
MLPF4	2.14		15	2.45	20
MLPF5	3.01		25	7.21	30
MLPF6	2.22		20	2.56	40
MLPF7	2.71		10	3.92	15
MLPF8	2.39		30	2.69	60
MLPF9	2.04		35	2.67	15
MLPF10	2.69		15	2.95	40
P301	2.75		35	3.92	20
PLPF	2.20		40	2.90	25
50%P301	2.31		50	—	—
50%PLPF					
25%P301	2.50		90	—	—
75%PLPF					

^a Separates into two phases unless vigorously stirred.

lolation of the lignin increased the reactivity of the resin prepared from it.

Pine and eucalyptus plywood boards manufactured using the resins prepared in this work met the EN 314-1:1993 standard for WBP quality boards, and afforded knife test results similar to those of boards manufactured with a commercial phenol-formaldehyde resin. The LPF resins spread better than the commercial resin, and the presence of lignin reduced the occurrence of blowouts. Best results were obtained by mixing a modified LPF resin with a commercial phenol-formaldehyde, each component of the mixture correcting the deficiencies of the other.

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