

Use of a Methylolated Softwood Ammonium Lignosulfonate As Partial Substitute of Phenol in Resol Resins Manufacture

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ABSTRACT: The synthesis of lignin-phenol-formaldehyde (LPF) was studied to determine its optimum operating conditions. The lignin proposed as phenol substitute has been the softwood ammonium lignosulfonate. The resin synthesis was optimized by varying the methylolated lignosulfonate content, 18–52%; the sodium hydroxide to phenol-modified lignosulfonate molar ratio, 0.3–0.94; and the formaldehyde to phenol-modified lignosulfonate molar ratio,

1.1–3.5. The parameters employed in the characterization of LPF resins were free phenol, free formaldehyde, gel time, alkaline number, viscosity, pH, solid content, and chemical structure changes. The properties of LPF resin comply with the requirements for its utilization in plywood manufacture. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 643–650, 2004

Key words: resins; synthesis; adhesives

INTRODUCTION

Environmental and ecological concerns have increased the attention paid by the chemical industry to renewable raw materials. Lignin is a wood-derived material, which is obtained as a by-product in the pulp industry. The chemical structure of lignin is similar to that of phenol, making it an interesting alternative to replace phenol in phenol-formaldehyde (PF) resin formulation.¹ Together with availability and low toxicity, lignin cost can be lower than that of phenol and does not depend on oil prices.

Lignin can be obtained by different pulping processes but only lignosulfonates are available in great quantities. Among them, ammonium lignosulfonates have been reported to be the most adequate to formulate PF resins.^{2,3} The main reasons include the fact that the phenolic resins with incorporation of ammonium lignosulfonates have better properties than those formulated with calcium or sodium lignosulfonates.⁴ Besides, ammonium lignosulfonate is soluble in several organic solvents, whereas calcium, magnesium, and sodium salts are only soluble in water. However, there are some authors that employ the calcium lignosulfonates owing to the fact that they are, in general, cheaper than the others.⁵ Another important aspect for the lignosulfonates selection is their source. Thus, the soft-

wood materials are more suitable for their utilization in the formulation of resol PF resins because they have more reactive sites in the aromatic ring than those coming from hardwood lignosulfonates.

In the early studies on this subject pure lignins were incorporated to phenolic resol resins applied to wood adhesives. The current trend is to modify the chemical structure of the lignins to increase their reactivity toward formaldehyde.⁶ The modification can be accomplished by different methods: methylation, phenolation, demethylation, and fractionation.^{3,7,8} Methylation and phenolation are the most interesting methods to modify the lignin because they are cheap and the natural polymer increases its reactivity. However, the demethylation reaction is very expensive and the fractionation process only separates fractions of lignin but does not increase its reactivity.

In some cases, the incorporation of modified organosolv lignin in resol resins was studied.^{9–12} When the organosolv lignin is methylolated with formaldehyde, the resulting product can substitute up to 50% of the phenol in the PF resol without loss of its properties.¹¹ Other authors obtained substitutions of phenol by lignin between 20 and 40% in the resol resins destined for plywood manufacture.^{13,14} The formulated resol resins with Kraft lignin or lignosulfonate have been less studied.^{3,15–18} Olivares¹⁹ obtained resins with 20% of phenol replacement by Kraft lignin for its application in particleboard. Klasnja and Lopitovic²⁰ replaced up to 50% of the phenol by Kraft lignin or lignosulfonate in the phenolic resol resins,

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TABLE I

Run	F/PL	S/PL	L (%)	P _f (% w)	pH	an	t _{gel} (min)	F _f (% w)	μ (cP)	SS (%)
1	1.6	0.8	45	11.0	12.2	232.1	34	1.2	78.6	54.6
2	3.0	0.8	25	0.3	11.6	202.6	12	1.3	364	55.9
3	1.6	0.4	45	0.7	11.0	138.9	10	1.5	1300	52.8
4	3.5	0.6	35	0.01	10.4	122.5	2	2.1	—	55.8
5	2.3	0.6	35	0.7	11.4	172.0	9	1.3	621	55.1
6	1.6	0.4	25	1.8	11.1	150.4	11	0.8	671	52.8
7	3.0	0.4	25	0	10.7	83.1	0	1.3 ^a	—	38.2 ^a
8	2.3	0.3	35	0	10.3	73.6	0	1.2 ^b	—	37.7 ^b
9	1.6	0.8	25	10.4	12.2	257.1	23	0.8	83.5	56.8
10	2.3	0.6	18.2	0.7	11.4	184.7	10	0.8	655	53.9
11	2.3	0.6	51.8	0.6	11.3	151.2	12	1.5	222	53.4
12	2.3	0.6	35	0.4	11.3	171.5	9	1.1	875	54.9
13	1.1	0.6	35	8.9	11.9	236.6	21	0.7	111	55.1
14	3.0	0.8	45	0.3	11.2	167.8	10	1.4	494	56.5
15	2.3	0.6	35	0.41	11.3	179.1	10	0.9	621	54.8
16	2.3	0.94	35	4.4	11.9	235.8	21	0.7	119	57.5
17	3.0	0.4	45	0	10.6	72.7	0	0.7 ^c	—	35.3 ^c

Note. Reaction time: 180 min (a); 205 min (b); and 105 min (c).

which have good strength properties. On the contrary, Pranda²¹ indicated that the mechanical resistance of the resin as adhesive can be reduced by the lignin content.

Total consumption for phenolic resins in the world amounted to more than 2.9 million tons in 2001.²² The largest users of phenolic resins are the plywood and reconstituted wood products industries, which employ mainly resols. This shows the importance of this field.

In this work, softwood ammonium lignosulfonates modified by methylation have been proposed as phenol substitutes in the synthesis of PF resins for the production of wood panel adhesives. The softwood ammonium lignosulfonate, chosen for the reasons mentioned above, was methylated because this reaction is carried out in alkaline medium, as the formulation of resol phenolic resins. This paper deals with the study of the lignin-phenol-formaldehyde (LPF) resol resin formulation. To achieve this objective, the optimum operating conditions of LPF resin were determined for attaining a thermosetting polymer similar to commercial PF resol resins.

EXPERIMENTAL

A commercial resol phenolic resin was supplied from Bakelite Ibérica (Spain) and tested in this study. This product is obtained by the polymerization between phenol and formaldehyde in alkaline medium. LPF was synthesized in the laboratory with a methylated softwood ammonium lignosulfonate. The methylation conditions were reported in a previous work.²³ First, methylated lignosulfonate, phenol, and sodium hydroxide were dissolved in 60 mL of water and

heated to 80°C. Then, the formaldehyde (37%, wt) was added in six equal shares at intervals of 15 min. The reaction time was fixed in 5 h. Finally, the resin was distilled to adjust both its solids content and its viscosity.

The variables and ranges studied were content of methylated ammonium lignosulfonate (L = 25–45%), sodium hydroxide to phenol-modified lignosulfonate molar ratio (S/PL = 0.4–0.8), and formaldehyde to phenol-modified lignosulfonate molar ratio (F/PL = 1.6–3.0).

The response surface method employed is based on a 2³ central composite experimental design.²⁴ The axial point distance corresponds to a rotatable design. The experimental matrix design is shown in Table I, where the experimental results for all responses can also be found. The sequence for the experimental work was randomly established to reduce the influence of systematic errors on the interpretation of results. The equations used to correlate the experimental results were of the form

$$Z = a_0 + a_f f + a_s s + a_L L + a_{fs} fs + a_{fL} fL + a_{sL} sL + a_{ff} f^2 + a_{ss} s^2 + a_{LL} L^2, \quad (1)$$

where Z is the response considered and a_{ij} are regression coefficients. From the analysis of variance (ANOVA), an F test at the significance level of 5% was used to identify insignificant effects. Both ANOVA and regression models were carried out with Statgraphics 5.0 software package. The analysis of lignin-phenolic resol properties (model responses) has been carried out using the following methods.

Free phenol

Free phenol (P_f) concentration was determined by gas chromatography using a Varian 3400 chromatograph with a flame ionization detector and helium as carrier gas. An HP-INNOWax (crosslinked polyethylene glycol) high-performance capillary column of 0.2 μm film thickness, 50 m length, and 0.2 mm internal diameter was used. The internal standard employed was *p*-cresol, which was added to the methanol dissolved samples.

Gel time

The apparatus employed for the measurement operates in accordance with ISO 9396 B. A test tube equipped with a plunger was filled with 10 g of lignin-phenolic resin and then placed in a constant temperature bath (130°C). The plunger was moved up at short intervals. When the gel point (t_{gel}) was reached, the test tube was lifted with the plunger, stopping a clock.

Alkali number

The employed method to determine alkali number is based on the Bakelite operating mode. The resin is dissolved in a mixture of acetone-water (1:1, v/v) and titrated with 0.1 N hydrochloric acid to pH 5.

Free formaldehyde

Free formaldehyde (F_f) was determined by the hydroxylamine hydrochloride method with end point titration (ISO 9397). The lignosulfonate (1 mg) was dissolved in 60 mL of isopropanol-water mixture (2:1, v/v) and hydrochloric acid was added until pH 2–3. Sodium hydroxide (0.1 N) was used to adjust the pH to 3.5. Finally, 10 mL of a hydroxylamine-hydrochloride solution (10%, w,w) was added. After 10 min, the resultant solution was retitrated with 0.1 N sodium hydroxide to pH 3.5.

Viscosity

The viscosity of liquid resol resin, thermostated at 25°C, was measured in a Brookfield viscosimeter at 30 rpm with a spindle (No. 3).

Solids content

Solids content was measured by gravimetry. The resin was weighed before and after drying at 150°C for 30 min.²⁵

Structural changes

¹³C-NMR spectroscopy was employed to characterize the resin structures. Lignin-phenolic and phenol-formaldehyde resins spectra were recorded on a 500-MHz NMR spectrometer (Bruker AMX 500). The following conditions were used: 4000-Hz sweep width, 7.2- μs pulse width, and a temperature of 297 K. A total of 0.1 g of sample and 10 μL of tetramethylsilane (TMS) were dissolved in 1 mL of deuterated dimethylsulfoxide (DMSO_{d6}). ¹³C chemical shifts were measured with respect to TMS as internal standard $\{\delta(\text{DMSO}_{d6}) = 39 \text{ ppm}\}$. In the present work, the signals of the ¹³C-NMR spectra were assigned according to the literature.^{26,27}

RESULTS AND DISCUSSION

The responses analyzed for regression models, mentioned above, were free phenol (P_f), pH, alkaline number (AN), and gel time (t_{gel}). Free formaldehyde (F_f), viscosity (μ), and solid content (SS) of the LPF resins were also considered responses but they could not be modeled because in three runs solid resol resins are obtained before the reaction time, 5 h, is achieved. In this state, these resin properties cannot be measured and the gel time is considered zero. Operating conditions and results obtained are shown in Table I.

To determine the optimum operating conditions of lignin-phenolic resin formulation, the values of their different responses were compared with the properties of a commercial resol resin. The structure of optimum resin was also analyzed and compared with respect to the commercial PF resol resin.

The ANOVA *F*-distributions of free phenol, pH, alkaline number, and gel time are always lower than 18.58, which allows the rejection of the effects of these responses with a significance level lower than 95%. Thus, the following equations were obtained:

$$P_f(\%, w) = 2.91287 - 7.79832 \cdot f + 27.9959 \cdot s + 2.96478 \cdot f^2 - 16.3929 \cdot f \cdot s + 16.2779 \cdot s^2 \quad (2)$$

$$\text{pH} = 9.36705 + 0.384951 \cdot f + 5.54122 \cdot s - 0.00550803 \cdot L - 0.103908 \cdot f^2 - 0.714286 \cdot f \cdot s - 1.3944 \cdot s^2 \quad (3)$$

$$\text{AN} = 100.087 - 46.4217 \cdot f + 464.299 \cdot s - 1.01123 \cdot L - 178.208 \cdot s^2 \quad (4)$$

$$t_{\text{gel}}(\text{min}) = -5.113357 - 0.77048 \cdot f + 40.8735 \cdot s + 0.20106 \cdot L + 1.43045 \cdot f^2 - 12.5 \cdot f \cdot s - 0.214286 \cdot f \cdot L + 0.625 \cdot s \cdot L, \quad (5)$$

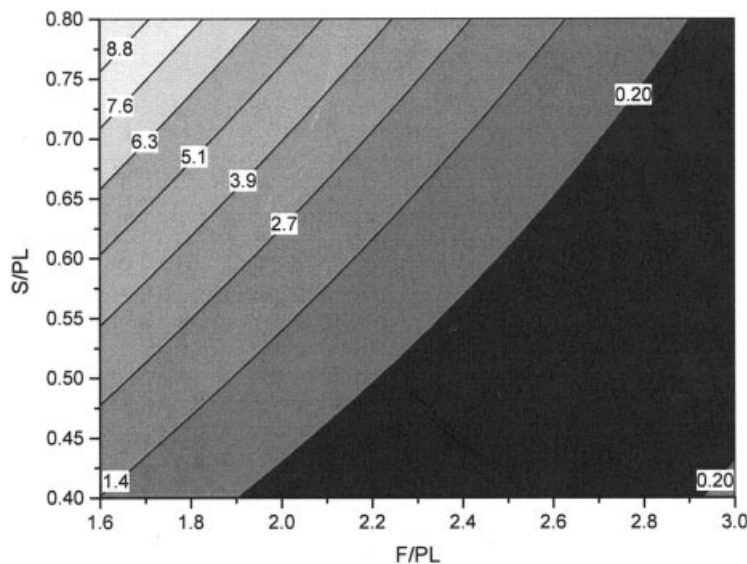


Figure 1 Contour map for free phenol depending on both S/PL and F/PL.

where f is the F/PL molar ratio, s is the S/PL molar ratio, and L is the methylolated softwood ammonium lignosulfonate content.

Equations (2), (3), (4), and (5) show an important influence of the s factor. Equations (3) and (4) refer to pH and alkali number, respectively. These responses are strongly influenced by the sodium hydroxide content. In the case of phenol, Eq. (2), an increase in S/PL molar ratio favors the condensation reaction between phenol and formaldehyde and, therefore, the thermosetting polymer polymerization. But, if the S/PL molar ratio is too high, the Cannizzaro reaction predominates. Hence, formaldehyde reacts with itself and the condensation degree decreases during the reaction,

which produces a polymer with greater free phenol content and higher gel time, Eq. (5).

Figures 1, 2, and 3 show, respectively, the contour map of free phenol, pH, and gel time for a methylolated lignosulfonate content of 35% (w), as a function of both S/PL and F/PL molar ratios. Since the concentration of free phenol must be less than 0.2% because of its high toxicity, it can be seen from Figure 1 that it is necessary to operate in the black region. The effects of S/PL and F/PL molar ratios on the lignin-phenolic resin pH, shown in Figure 2, are not restrictive. The pH requirements for the resol resins manufacture are 9.5 or higher.^{18,20,28} The pH response is interesting because of its influence on the resin storage

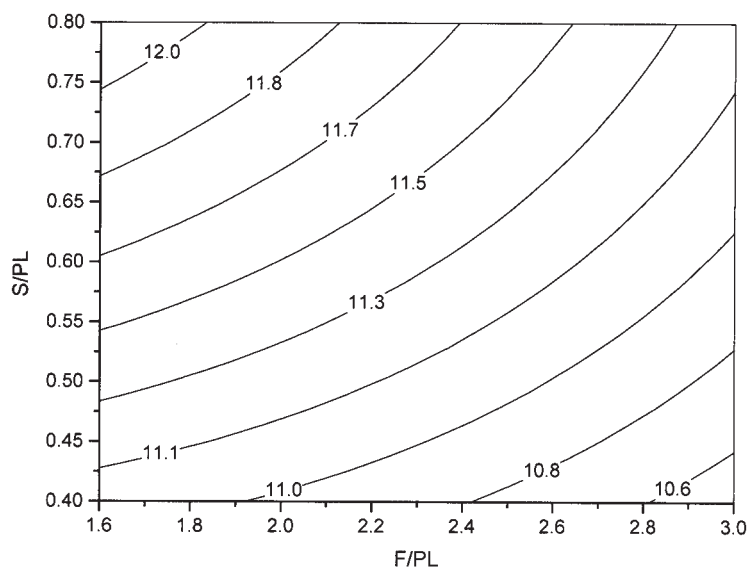


Figure 2 Contour map for pH depending on both S/PL and F/PL.

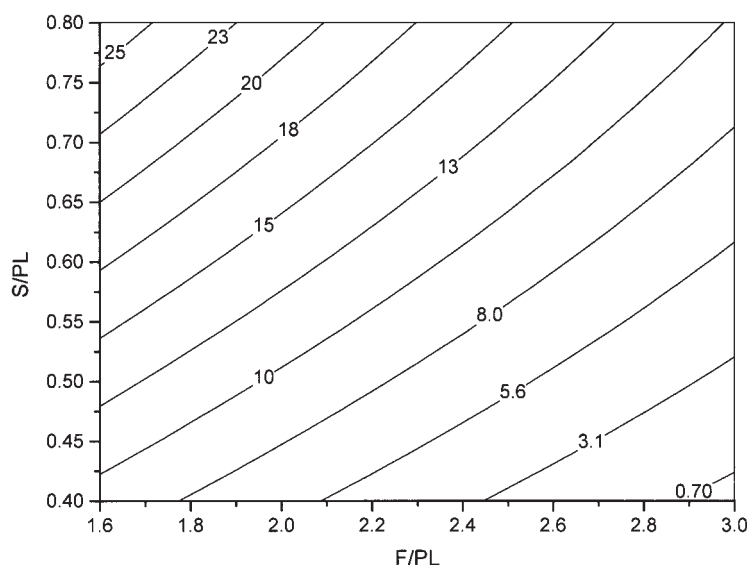


Figure 3 Contour map for gel time depending on both S/PL and F/PL.

life. The incorporation of a lignosulfonate in the resin formulation supposes a reduction of its pH compared to a commercial resin synthesized under the same conditions.

The alkaline number is another measure used to determine the alkalinity degree in the resol resin. Obviously, its value is determined by the same operating conditions as the pH. In any case, the final pH or alkaline number of the formulated resol resin can be adjusted by a further sodium hydroxide addition.

The gel time response represented in Figure 3 has an operating zone between 8 and 10 min, because a higher or lower value leads to a slow or fast cure, respectively. If the cure is slow, the manufacture of the plywood is very expensive, while a very fast cure could cause bad properties on the board.

The effect of lignosulfonate content on the formulation of LPF resins for the commented responses is as follows: the free phenol response is not influenced by the lignosulfonate content, as can be seen in Eq. (2). In the case of pH and alkaline number, which have the same behavior, an increase of lignosulfonate in the LPF resin formulation gives rise to a slight decrease of pH. The gel time, in general, decreases with high lignosulfonate content, low S/PL, and high F/PL molar ratios. The methylolated lignosulfonate content more suitable for incorporate in the formulation of phenolic resol resins is 35% (wt).

The values of free formaldehyde response are, in the studied range, higher than 0.2% (wt), which is the maximum value acceptable by environmental reasons. It is not possible to reach these low values as a result of the use in excess of the formaldehyde in the formulation of the resins. However, the content of formaldehyde can be reduced up to specifications by urea addition.

Figure 4 shows the relation between the free formaldehyde content and the gel time values of 17 runs. As mentioned before, the suitable gel time must be included between 8 and 10 min; hence, it is necessary to operate simultaneously with both molar ratios (F/PL and S/PL) in their high, intermediate, or low levels. Therefore, the operating conditions have an important influence on these two responses. The formaldehyde content of final product is adjusted by urea addition.

The values of viscosity depend on the operating conditions in the formulation of lignin-phenol-formaldehyde resins. The obtained results are in a wide viscosity range of 38–1300 cP (Table I). The resins with a high phenol content have a low condensation degree. Thus, the low viscosity values are obtained gel

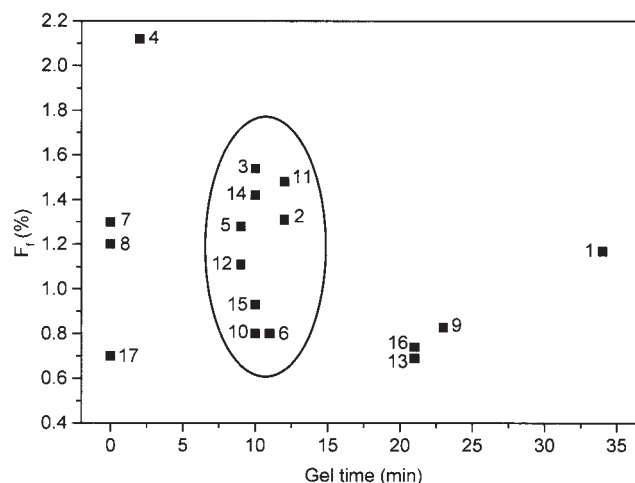


Figure 4 Variation of gel time in relation to free formaldehyde.

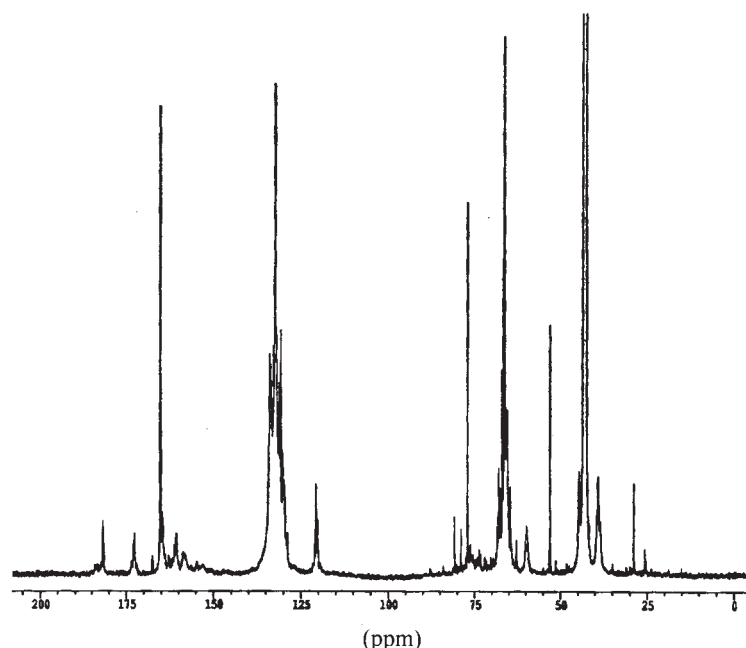


Figure 5 ^{13}C NMR spectrum of optimum LPF resin.

times > 20 min. This circumstance is caused by the high sodium hydroxide concentration, which allows that the formaldehyde reacts with itself through the Canizzarro reaction.²⁹

For resol PF resin adhesive formulation, it is recommended that the viscosity of resin range is between 275 and 425 cP. This adhesive is employed for plywood manufacture. The viscosity drops off when urea is added upon lignin-phenolic resin for reducing its formaldehyde content. The urea addition produces the rupture of hydrogen bridges in the lignin-resol resin,³⁰ so that the LPF resins are necessarily synthesized with viscosities greater than 600 cP.

According to the above comments, the optimum operating conditions to formulate a lignin-resol resin are 35% (wt) modified lignosulfonate content, F/PL and S/PL molar ratios of 2.5 and 0.6, respectively, and 3% urea respect to total weight of resin. Under these operating conditions, the levels of free phenol and free formaldehyde in LPF resins resulted in less than 0.2% (wt). The gel time, viscosity, pH, and solid content of the LPF resin are, respectively: 8 min, 360 cP, 11.3, and 52–57% (wt). The LPF resin gel time is similar to that of commercial resin (9–10 min), which indicates a further suitable cure. The value of viscosity of LPF resin is within the range 275–425 cP.

The LPF resin has a lower pH than that of commercial resin because lignosulfonate decreases it. Its value can be adjusted once the resin has been formulated. The results of solids content are in agreement with the range of commercial resin: 45–47% (wt). This response and viscosity can be increased by the LPF resin distillation. The other properties do not change using this procedure.

The following stage of experimentation focused on the comparison between the chemical shifts and chemical structures of lignin-phenolic and commercial resins. In Figures 5 and 6, where the ^{13}C -NMR spectra of both resins are represented, it can be seen that the DMSO peaks are shifted 3–4 ppm with respect to its original position (39.5 ppm). However, in this paper the peaks of the spectra are referred to the original chemical shifts.^{26,27}

From Figure 5, it can be seen that the lignin-phenolic resin shows an *ortho* substitution of the methylol group ($-\text{CH}_2\text{OH}$) at 115 ppm, while *para* carbon is unsubstituted at 120 ppm during the methylolation reaction. The methoxyl group (55.6 ppm) is not detected because these groups have been substituted by the methylol groups in the aromatic rings of the modified lignosulfonates. The incorporation of methylolated lignosulfonate in the formulation of phenolic resins involves the presence of new peaks. Carbonyl groups are observed in the unsaturated C_α and C_β of the lignosulfonate at 181 ppm and chemical shifts of unsaturated C_α and C_β carboxyl groups at 173 ppm. The phenoxy carbons are alkylated so *ortho* as *para*, which occurs at 151.2–156.4 ppm.

Figure 6 shows a ^{13}C -NMR spectrum of a commercial PF resin. The chemical shifts of the *ortho-ortho'* methylene link are not observed due to the fact that these links are not favored in presence of sodium hydroxide.²⁷ The *ortho-para'* methylene links appear in a significant amount at 35.8 ppm, whereas *para-para'* methylene links are not detected because they overlapping with the solvent peak (DMSO). The LPF resin is a more complex thermoset than the PF resin due to the presence of lignosulfonates. In any case, both res-

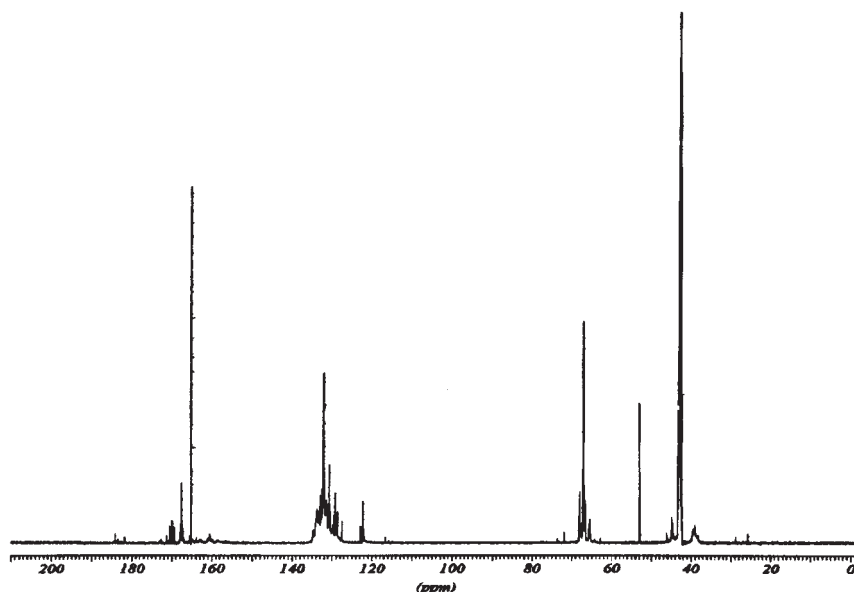


Figure 6 ^{13}C NMR spectrum of commercial PF resin.

ins present peaks such as substitution of the methylol group or monomers linked through methylene bridges, which indicates the condensation degree of the resol resin, typical signals of this type of polymers.

The properties of LPF resin formulated under the conditions obtained comply with required specifications for its utilization as adhesive in the plywood manufacture. Obviously, to evaluate whether the substitution proposed is feasible, it would be necessary to undertake a new study to determine the behavior of the plywood adhesive prepared from the LPF resin.

CONCLUSION

The synthesis of a lignin-phenolic resin has been developed to conform to the existing production of commercial phenolic resin. The utilization of lignosulfonate in the PF resins is approached in two steps. Initially, the ammonium lignosulfonate is modified by methylation and immediately after natural polymer is incorporated into the resin formulations.

The optimum operating conditions of the LPF resin formulation are S/PL and F/PL molar ratios of 0.6 and 2.5, respectively, and 35% (wt) of replaced phenol by methylolated softwood ammonium lignosulfonate. Under these conditions, the analysis of the LPF resin formulated has similar characteristics to that of the commercial PF resol resin (reference sample). Therefore, the properties of LPF resin comply with required specifications for its utilization in the plywood manufacture.

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