

Preparation and Characterization of Phenol-Formaldehyde Resins Modified with Alkaline Rice Straw Lignin

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Phenol-formaldehyde (PF) is a thermosetting resin that is widely used in many fields. One of its important applications is as an adhesive for wood-based panels manufacturing. In this research work, modified phenol-formaldehyde resins were prepared using hydroxymethylated alkaline rice straw lignin as a substitute for petroleum-based phenol in the range of 20 to 50% by weight. The molar ratios of sodium hydroxide to phenol-modified alkaline lignin and the formaldehyde to phenol-modified alkaline lignin were from 1.0 to 1.4, and 1.8 to 2.6, respectively. The parameters used to characterize the modified phenol-formaldehyde resins were: free-formaldehyde, gel time, viscosity, pH, and solid content. The structural differences and similarities between the prepared resins were determined by FTIR spectroscopy. Results obtained were discussed according to the requirements for adhesives utilization in plywood manufacture, and the optimum operating conditions were selected. Infrared spectra of lignin-based phenol formaldehyde (LPF) resins showed structural similarity with that of PF resin.

Keywords: Adhesives; Hydroxymethylation; Lignin; Phenol formaldehyde; Wood panels

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INTRODUCTION

Phenol formaldehyde resin (resole type) is the most useful thermosetting resin for the manufacture of wood-based panels such as plywood, particleboard, and fiberboard (Nimz 1983; Sellers 1995; Gardziella *et al.* 2000; Zhang *et al.* 2013; Zhao *et al.* 2016). This resin has good chemical resistance, electrical insulation, and dimensional stability, but the price and environmental concerns may limit usage in some applications. The partial substitution of phenol by fillers or extenders is one way to reduce the price of these resins. Lignin is a good candidate to replace phenol in the phenol formaldehyde resins' formulation because (a) its polyphenolic structure is similar to that of phenolic resin (Fig. 1) (Forss and Fuhrmann 1979), (b) the material comes from renewable resources, and (c) it can be used as a macromolecular material without previous treatment (Nimz 1983; Pang *et al.* 2017).

Lignins are currently produced by several pulping and ethanol processes, but only liginosulfonates and kraft lignin are available in large quantities (Gosselink *et al.* 2004;

Vishtal and Kraslawski 2011). By contrast, organosolv lignin, hydrolysis lignin, and soda lignin are produced in minor quantities. In this last group, only the soda lignins have a short-term potential for industrial availability. The alkaline lignins have been reported to be the most adequate to formulate phenol formaldehyde resins because they are structurally similar to phenol-formaldehyde resins and contain large molecules that allow quick gelation (Forss and Fuhrmann 1979; Allan *et al.* 1989; Peng 1994). However, it was reported that lignins present some certain limitations, such as the lower number of reactive sites, low phenolic hydroxyl groups, and the steric impediments. For that, the unmodified lignins are relatively reluctant to undergo either self-condensation or condensation with formaldehyde, phenol, or phenol formaldehyde prepolymer (Vázquez *et al.* 1999).

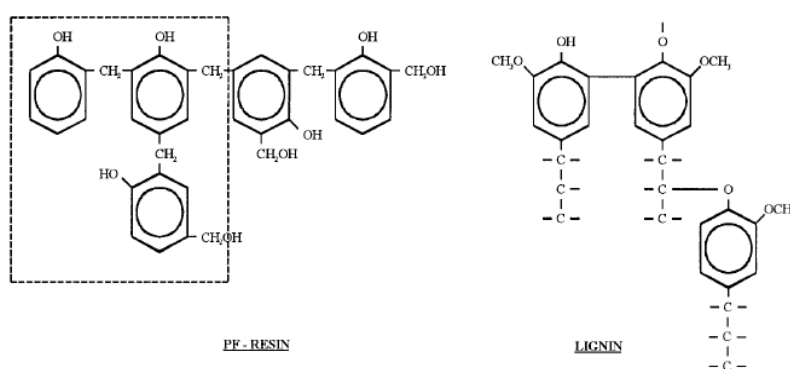


Fig. 1. Structure of PF resin and lignin (Forss and Fuhrmann 1979)

In the early studies related to the use of lignin for phenolic resins manufacturing, different types of unmodified lignins, which were obtained directly from the pulping liquor, were investigated. However, a current trend is to use modified lignins in order to increase their reactivities towards formaldehyde (Alonso *et al.* 2001; El Mansouri *et al.* 2006, 2007; Hu *et al.* 2011; Mancera *et al.* 2011; Jung *et al.* 2015; Fernandez-Rodriguez *et al.* 2017). There are several modification methods such as demethylation, reduction, oxidation, and hydrolysis that have been studied to improve the reactivity of lignin as well as to produce phenolic compounds from lignin (Hu *et al.* 2011; Diop *et al.* 2015; Ma *et al.* 2016; Norambuena *et al.* 2016; Li *et al.* 2018). Among all of the modification treatments that increase reactive sites in lignin, the phenolation and hydroxymethylation modifications are the most studied and effective for formulation of phenolic resins (Nada *et al.* 1987; Allan *et al.* 1989; Sellers *et al.* 1994; Alonso *et al.* 2004 and 2005; Yang *et al.* 2014; Podschun *et al.* 2015; Jiang *et al.* 2018). The modified lignin from these later methods could partially replace phenol in phenol-formaldehyde resin synthesis.

Some of the lignins that have been used in phenolic resins are derived from annual plants such as flax (Tejado *et al.* 2007, 2008), or kenaf (Yan 2009), and agricultural waste such as sugar cane bagasse and wheat straw (Hoareau *et al.* 2006; Ghorbani *et al.* 2016; Tachon *et al.* 2016). However, there has been little research published on the preparation and characterization of phenol formaldehyde resin using alkaline rice straw lignin. Thus, the main objective of this work is to prepare and characterize a modified phenol-formaldehyde resins using hydroxymethylated alkaline lignin from rice straw as a substitute of petroleum-based phenol. The prepared resins

were characterized, and the obtained results were discussed according to the specifications of resins applied for plywood manufacturing.

EXPERIMENTAL

Materials

The alkaline lignin (AL) used for the preparation of hydroxymethylated lignin was supplied by South China University of Technology, Guangzhou, China. This lignin was produced by ShangDong QuanMing Paper Making Co. Ltd. by the alkaline process using sodium hydroxide and Na_2CO_3 from rice straw.

This lignin was purified by its treatment with sulfuric acid (1%) several times and washed extensively with hot water to remove the inorganic substances and solubilize the residual sugars (El Mansouri *et al.* 2006 and 2011a). The formaldehyde (35 to 40% aqueous solution) and phenol (99%), used in this work were purchased from Sigma Aldrich and used as received.

Hydroxymethylation of Lignin

Lignin powder was slowly added to NaOH solution, keeping the pH of the mixed solution between 12 and 13 for better dissolution of the lignin powder, which was facilitated by vigorous stirring with an overhead stirrer. A molar ratio of NaOH to lignin of 0.8 was used, which resulted in a final pH of 12.3. A glass flask equipped with a condenser, a thermometer, and an overhead stirrer was charged with the above solution, and then formaldehyde aqueous solution was added according to the molar ratios of formaldehyde to lignin of 1.0.

The obtained mixture was heated to 50°C and kept at this temperature for 8 h according to the optimum conditions reported in our previous research works on lignin hydroxymethylation (El Mansouri *et al.* 2011b).

Synthesis of Phenol-formaldehyde Resins

The prepared hydroxymethylated lignin was copolymerized with phenol and formaldehyde at 80 °C in a glass flask equipped with a condenser, a thermometer to control temperature, and an overhead stirrer. A total of 11 lignin-phenol formaldehyde (LPF) resins, as indicated in Table 1, were prepared by varying the replacement percentage of phenol by hydroxymethylated lignin (%L) between 20 and 50%, the mass ratio of formaldehyde/(phenol+lignin) [$F/(P+L)$] between 1.8 and 2.6, and the ratio of sodium hydroxide/(phenol plus lignin) [$S/(P+L)$] between 1.0 and 1.4. A 2x2x2 factorial design with a three repeated central points was applied in order to quantify the effect of those parameters on the resins properties. The reaction was monitored by measuring the viscosity at 25°C with viscosimeter and halted when the resin viscosities reached 300 to 400 mPas. The obtained resins were cooled and stored at lower temperature pending to analysis. The diagram of the entire experimental protocol is shown in Fig.2.

Resins Characterization

The prepared resins were characterized according to gel time, solids content, viscosity, and free formaldehyde. The values for these parameters must be in agreement with commercial resins specifications applied for plywood.

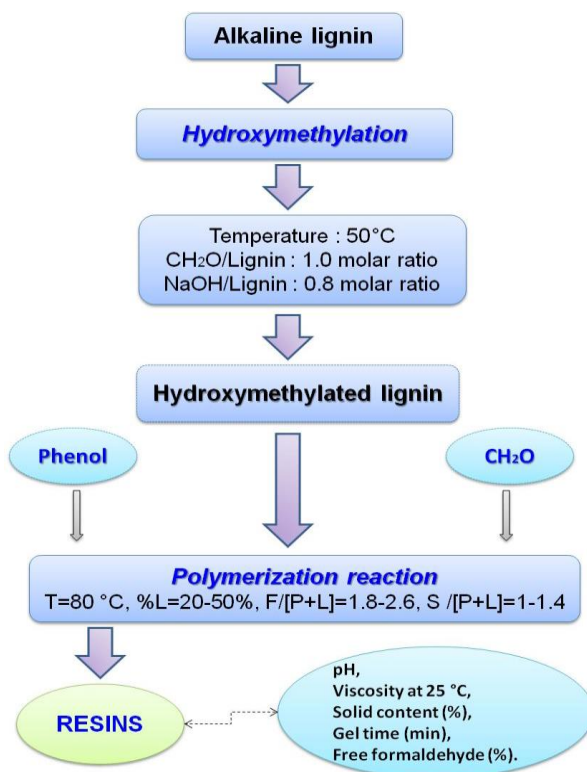


Fig. 2. Diagram of the experimental protocol

Gel Time

The used apparatus for gel time determination operates in accordance with ISO 9396 B. A test tube equipped with a plunger was filled with 10 g of unmodified and modified phenolic resins and then placed in an oil bath under a constant temperature of 130°C. The resin was mixed at short time intervals and the gel point was reached when the plunger could not be moved up.

Solid Content

Solid content was determined by gravimetry from the weighted amount of resin before and after drying the resin samples at 150 °C for 30 min.

Viscosity

The viscosities of both unmodified and modified liquid phenol formaldehyde resin resins were determined using a Brookfield viscosimeter at 30 rpm at 25 °C.

Free Formaldehyde

Free formaldehyde was determined by the hydroxylamine hydrochloride method with end-point titration (ISO 9397). The modified phenol formaldehyde resins were

dissolved in isopropanol-water mixture (2:1, v/v) and hydrochloric acid was added until pH was in the range 2 to 3. The 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 0.1N sodium hydroxide to pH 3.5.

FTIR-spectroscopy

FTIR spectroscopy was employed to characterize the structure of the lignin raw material and the prepared modified phenolic resins. FTIR spectra were recorded with a Nicolet 5700 FTIR-spectrophotometer, using the KBr pellet method. The acquisition conditions were: spectral width of 4000 to 400 cm^{-1} , 32 accumulations, and 4- cm^{-1} resolution. The pellets were prepared with a mixture of 300 mg potassium bromide and 5-10 mg of analyzed samples.

RESULTS AND DISCUSSION

The results of the characterization of modified phenolic resins, including pH, gel time, viscosity at 25 °C, solids content, and free formaldehyde, are recorded in Table 1 together with the experimental conditions. Table 2 lists the results of fitting the data for pH (Y_1), gel time (Y_2) and viscosity (Y_3) with polynomials of the form (Eq. 1),

$$Y_j = a_{0j} + a_{1j} X_1 + a_{2j} X_2 + a_{3j} X_3 + a_{12j} X_1 X_2 + a_{13j} X_1 X_3 + a_{23j} X_2 X_3 + a_{123j} X_1 X_2 X_3 \quad (1)$$

where X_1 , X_2 , and X_3 are the values of $L(\%)$, $[F/(P+L)]$, and $[S/(P+L)]$, respectively after normalization to the interval $[-1,1]$. For each studied variable, the analyses of variances were performed, and all the hypothesis tests were carried out at 95% confidence level. The statistical analysis was carried out by using *Statgraphics 18 Centurion*.

Table 1. Experimental Conditions and Properties of Synthesized Modified Phenol Formaldehyde Resins

Samples	%L	F/ (P+L)	S/ (P+L)	pH	Solids (%)	Viscosity μ 25 °C (mPa.s)	Gel time (min)	Free CH ₂ O,%
LPF1	20	1.8	1.0	11.70	42.5	420	11.0	0.04
LPF2	50	1.8	1.0	10.20	41.3	330	10.2	0.03
LPF3	20	2.6	1.0	11.42	41.9	470	11.3	0.07
LPF4	50	2.6	1.0	10.92	41.5	790	12.0	0.10
LPF5	20	1.8	1.4	13.10	43.2	450	8.0	0.05
LPF6	50	1.8	1.4	12.40	42.6	370	11.0	0.06
LPF7	20	2.6	1.4	13.30	44.2	330	8.0	0.12
LPF8	50	2.6	1.4	12.25	43.0	500	10.0	0.10
LPF9	35	2.2	1.2	12.50	44.0	400	10.5	0.04
LPF10	35	2.2	1.2	12.56	44.2	430	10.3	0.03
LPF11	35	2.2	1.2	12.60	44.3	420	10.3	0.03

The fitted model for pH gave an R^2 value of 89.7% and a standard deviation of residuals (SDR) of 0.55. The analysis of variance reported in Table 3, showed that pH was significantly influenced only by (S/PL) at the $p=0.05$ significance level. The modeled response surface (Fig. 3) shows that for $L=35\%$, the pH increased with increase of (S/PL) molar ratio. The pH requirements for the resol resins were 9.5 or higher. This variable is of interest because of its influence on the resin storage life. In any case, the final pH of the synthesized resol resins can be corrected by addition of base or acid solution.

Table 2. Results of Fitting Eq. 1 to the Experimental Data for pH (Y_1), Gel time (Y_2), and Viscosity (Y_3)

Regression coefficients	$Y_1(\text{pH})$	$Y_2(\text{gel time})$	$Y_3(\text{viscosity})$
a_{0j}	12.0864	10.2364	446.36
a_{1j}	-0.4687	0.6125	40.00
a_{2j}	0.0612	0.1375	65.00
a_{3j}	0.8512	-0.9375	-45.00
a_{12j}	0.0812	0.0625	82.50
a_{13j}	0.0312	0.6375	-17.50
a_{23j}	-0.0487	-0.3875	-62.50
a_{123j}	-0.1687	-0.3125	-20.00

Table 3. Analysis of Variance for pH

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
$X_1:L(\%)$	1.7578	1	1.7578	5.83	0.0946
$X_2:F/PL$	0.0300	1	0.0300	0.10	0.7731
$X_3:S/PL$	5.7970	1	5.7970	19.23	0.0220
X_1X_2	0.0528	1	0.0528	0.18	0.7037
X_1X_3	0.0078	1	0.0078	0.03	0.8823
X_2X_3	0.0190	1	0.0190	0.06	0.8179
$X_1X_2X_3$	0.2278	1	0.2278	0.76	0.4487
Total error	0.9045	3	0.3015		
Total (corr.)	8.7968	10			

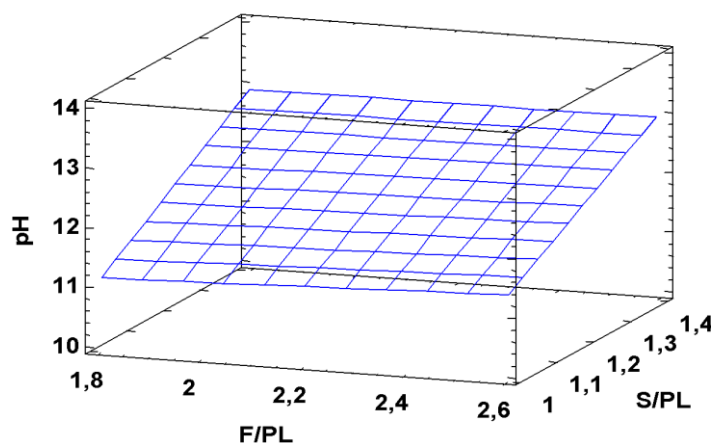


Fig. 3. Estimated response surface for pH at $L(\%)=35\%$, F/PL vs S/PL

The fitted model for gel time gave an R^2 value of 99.38% and a standard deviation of residuals (SDR) of 0.18. The analysis of variance (Table 4) showed that, at the $p=0.05$ significance level, gel time was significantly influenced by $[S/(P+L)]$ and $L(\%)$ together with the cross-terms $L(\%)*[S/(P+L)]$, $[F/(P+L)]*[S/(P+L)]$, and $L(\%)*[F/(P+L)]*[S/(P+L)]$. The modeled response surface (Fig. 4) shows that for $[F/(P+L)]=2.2$ molar ratio, the gel time increased with increase of lignin content at higher level of ($[S/(P+L)]=1.4$) molar ratio, and decrease with increase of $[S/(P+L)]$ molar ratio at lower level of lignin replacement ($L(\%)=20\%$). The same dependency of gel time on lignin content and $[S/(P+L)]$ molar ratio was reported by Alonso and Vázquez (Vázquez *et al.* 1999; Alonso *et al.* 2004).

A suitable gel time of modified phenol formaldehyde resins used for plywood manufacture must be included between 8 and 10 min. However, modified resins with gel time near to 10 min can be considered and tested for plywood manufacturing if they present low free formaldehyde content. According to this, LPF2 and LPF10 were selected to be tested for plywood manufacturing. The gel time is an important parameter to take into consideration when resins are formulated, because it determines the resins reactivities. The higher or lower values indicate a slow or fast curing reaction, respectively. A slow cure lead to longer pressing time, and therefore the manufacture of the plywood must be expensive. A very fast cure can cause the lost of the final properties of the board.

Table 4. Analysis of Variance for Gel Time

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
$X_1:L(\%)$	3.0012	1	3.0012	93.11	0.0024
$X_2:F/PL$	0.1512	1	0.1512	4.69	0.1189
$X_3:S/PL$	7.0312	1	7.0312	218.13	0.0007
X_1X_2	0.0312	1	0.0312	0.97	0.3974
X_1X_3	3.2512	1	3.2512	100.86	0.0021
X_2X_3	1.2012	1	1.2012	37.27	0.0088
$X_1X_2X_3$	0.7812	1	0.7812	24.24	0.0161
Total error	0.0967	3	0.0322		
Total (corr.)	15.5455	10			

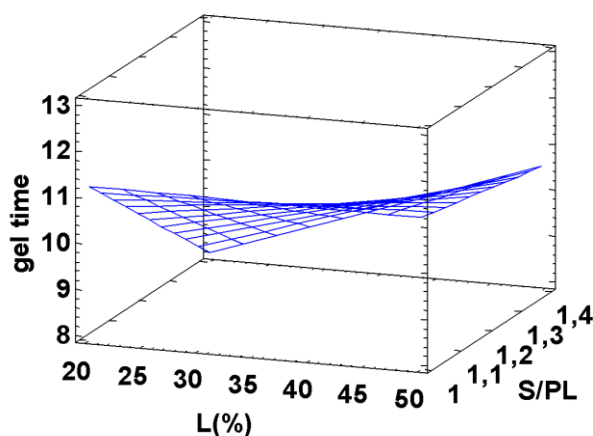


Fig. 4. Estimated response surface for gel time at $[F/(P+L)]=2.2$, $L(\%)$ vs. $[S/(P+L)]$

The fitted model for the viscosity gave an R^2 value of 97.40% and a standard deviation of residuals (SDR) of 37. Analysis of variance (Table 5) showed that viscosity was significantly influenced by all the studied parameters, and the cross-terms $(L(\%))*[F/(P+L)]$ and $[F/(P+L)]*[S/(P+L)]$ at the $p=0.05$ significance level. The modeled response surface (Fig. 5) shows that for $[S/(P+L)]=1.2$ molar ratio, the viscosity increased with increase of lignin content (in lower $[F/(P+L)]$ region) and $[F/(P+L)]$ molar ratio. The increase in viscosity of lignin-phenol formaldehyde resin with higher percent substitutions can be attributed to incorporation of high lignin content with a high molecular weight compared to phenol in the modified phenolic resins. In fact, the incorporation of a large amount of lignin with a high molecular weight is the main reason for increasing the molecular weight of final resin, thus resulting in higher viscosities for lignin-phenol formaldehyde resins. Previous research findings from Cheng *et al.*(2013) and Siddiqui *et al.*(2017) confirm a similar trend of increasing viscosities of lignin-based phenolic resins with increasing lignin replacement (Cheng *et al.* 2013; Siddiqui *et al.* 2017). Moreover, the increase in viscosity with the increase of F/PL ratio is attributed to the increase of degree of methylation as well as the branching of lignin-phenol formaldehyde resins, which should result in an increase of viscosity of the modified phenolic resins. Overall, the viscosity values obtained are between 330 and 790 (mPas), and most of the prepared resins have viscosities within the range of 275 to 425 (mPas) suitable for use in plywood manufacture (Alonso *et al.* 2004).

Table 5. Analysis of Variance for Viscosity at 25 °C

Source	Sum of Squares	D_f	Mean Square	F-Ratio	P-Value
$X_1:L(\%)$	12800.0	1	12800.0	9.36	0.0351
$X_2:F/PL$	33800.0	1	33800.0	24.70	0.0156
$X_3:S/PL$	16200.0	1	16200.0	11.84	0.0412
X_1X_2	54450.0	1	54450.0	39.80	0.0080
X_1X_3	2450.0	1	2450.0	1.79	0.2732
X_2X_3	31250.0	1	31250.0	22.84	0.0174
$X_1X_2X_3$	3200.0	1	3200.0	2.34	0.2237
Total error	4104.5	3	1368.2		
Total (corr.)	158255.0	10			

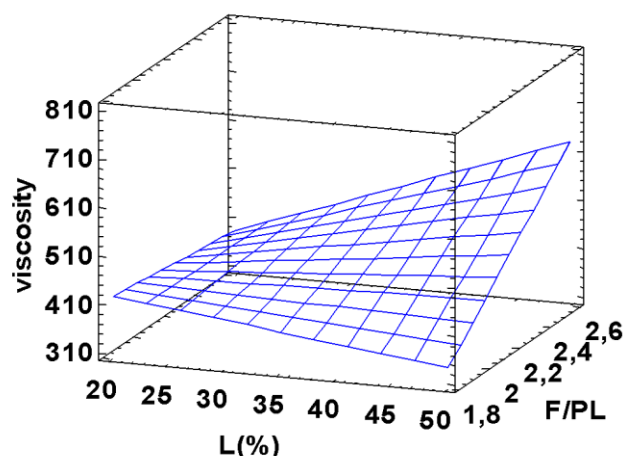


Fig. 5. Estimated response surface for viscosity at S/PL=1.2, L(%) vs F/PL

For the free formaldehyde content and solid content, the analysis of variances showed no significant dependence on the studied independent variables. The results obtained for solid content were between 41 and 45%. They were near to the range of values of the commercial resins used for plywood production, which ranges from 45 to 47% (Alonso *et al.* 2004). It is very important to point out that the solid content and viscosity of prepared modified phenol formaldehyde resins can be adjusted by resins distillation under vacuum while keeping other properties constant. In the case of free formaldehyde content, within the range of the three studied variables, the obtained values for formaldehyde content were lower than 0.2%, which is the maximum value acceptable for environmental reasons. The low values of free formaldehyde found for the formulated modified phenolic resins are in the same range of those reported in a previous study that reported values 0.02% and 0.12 % (Vazquez *et al.* 1999). When formaldehyde is used in excess, it is very difficult to reach low values of free formaldehyde in the formulation of lignin-phenol formaldehyde resole resins. In any case, the high free formaldehyde content can be lower than the desired value by urea addition.

FTIR-spectroscopy

Figure 6 shows the FTIR-spectrum of lignin raw material used for resins preparation. This spectrum is characterized by a broad band of OH stretching located at 3415 cm^{-1} , which is attributed to the hydroxyl groups in phenolic and aliphatic structures, and the bands at 2933 cm^{-1} and 2849 cm^{-1} , arising from CH stretching in the aromatic methoxyl groups and the methyl and methylene groups of the side chains. The absence of peaks at 1708 cm^{-1} and 1646 cm^{-1} is a characteristic of alkali soluble lignin fractions. These bands are assigned to C=O stretching in unconjugated ketone and carbonyl bond in ester group or in conjugated *p*-substituted aryl ketone, respectively (Khan and Ashraf 2005). The absorption bands at 1600 cm^{-1} and 1500 cm^{-1} are assigned to aromatic ring vibrations. The bands at 1455 cm^{-1} and 1425 cm^{-1} are due to the asymmetric C-H deformation in $-\text{OCH}_3$ groups. The bands at 1120 cm^{-1} is characteristic of aromatic C-H in S units of lignin molecule and the C-O of primary alcohol at 1044 cm^{-1} . All these bands match well with the literature values (Faix 1992).

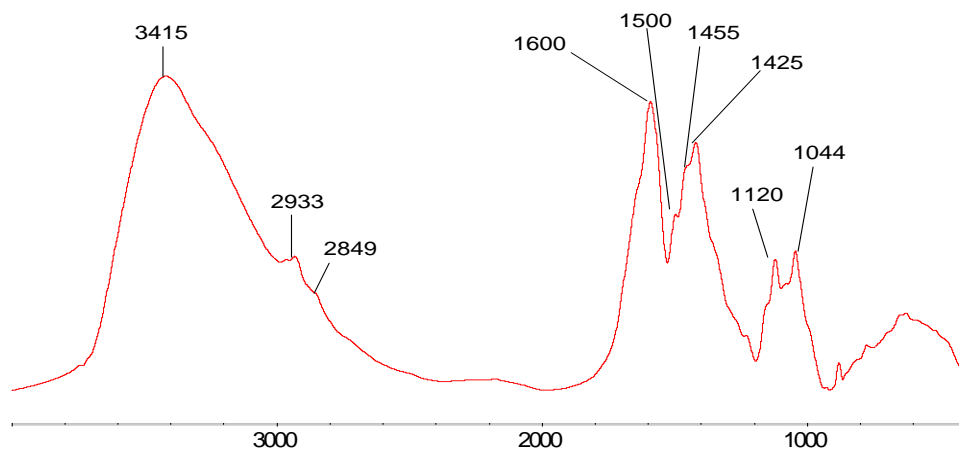


Fig. 6. FTIR spectrum of lignin raw material

The FTIR spectra of (a) unmodified (PF) and (b) modified (LPF) with $L=35\%$ and (c) $L=50\%$ are shown in Fig. 7. In the PF, a band at 3373 cm^{-1} was observed, which shows the presence of OH groups. This band, appearing at lower frequency, indicates strong hydrogen bonding occurs. Bands at 2937 cm^{-1} and 2846 cm^{-1} are the consequence of in-plane and out-of-plane stretching of aliphatic $-\text{CH}_2-$. Similarly, these bands are also present in LPF with 35% and 50% of lignin. This highest wave-number zone do not offer any difference among the three resins analyzed. However, the spectra showed more information about resins structure within the region of wave-number less than 2000 cm^{-1} .

The most typical band of lignin structures is 1600 cm^{-1} . In this case, it is present in LPF and it becomes more intense with increasing percentage of lignin in LPF resin from 35% to 50%. In PF the band at 1474 cm^{-1} is assigned to $-\text{CH}-$ deformation in $-\text{CH}_2-$ groups. Rocznik *et al.* (1983) identified the region between 1500 cm^{-1} and 1400 cm^{-1} as characteristic of deformation vibration of $-\text{CH}-$ bands in a $-\text{CH}_2-$ group, and they observed some difference from the spectra of resins. These differences can provide information as to the structure of methylene bridges. In the LPF the appearance of bonds at 1474 cm^{-1} and 1450 cm^{-1} indicates the presence of a methylene bridge. Moreover, the band at 1474 cm^{-1} is not very intensive in both LPF, which indicates that methylolated lignin molecule incorporates hydroxymethyl groups in the LPF (Nada *et al.* 1997; Alonso *et al.* 2001). The band observed at 1386 cm^{-1} in LPF is attributed to lignin, which is assigned to C-O of syringyl unit present in lignin. The band at 1269 cm^{-1} is attributed to in-plane vibration of C-O of the phenolic group present in PF and LPF. In PF the band at 1155 cm^{-1} and 1015 cm^{-1} are characteristic for in-plane deformation of aromatic C-H, whereas the band at 1154 cm^{-1} in LPF is attributed to C-H stretching in a syringyl unit and is attributed to presence of lignin. The band at 1018 cm^{-1} in LPF is characteristic of lignin and is attributed to the C-O of primary alcohol. The bands in the region of $850\text{ to }750\text{ cm}^{-1}$ are due to the trisubstituted benzene ring and confirm the formation of a three dimensional network structure.

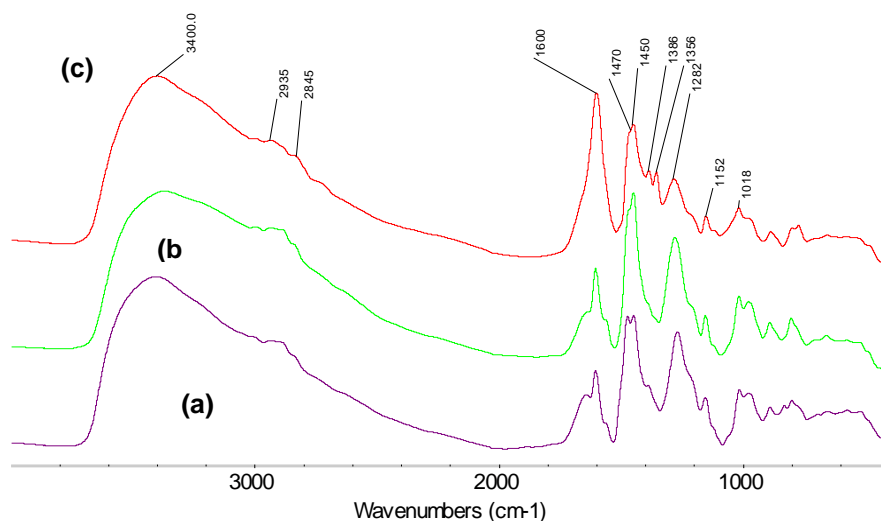


Fig. 7. FTIR-spectra of (a) PF, (b) LPF with $L=35\%$ (LPF10), and (c) LPF with $L=50\%$ (LPF2)

CONCLUSIONS

1. Different modified phenol formaldehyde resins were prepared and characterized using alkaline rice straw lignin structurally modified by hydroxymethylation reaction.
2. The modified phenol formaldehyde LPF2 and LPF10 with lignin content of 50% and 35%, respectively, were selected to be tested for plywood manufacturing because of their suitable gel time and low free formaldehyde content.
3. FTIR spectroscopy analysis showed that the spectra of LPF resins were structurally similar to that of the unmodified PF resin.
4. To evaluate the feasibility of the achieved lignin replacement, it is necessary to undertake complementary experiments to determine the properties of manufactured plywood from the prepared lignin-based phenolic resins.

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