Development and characterization of groundnut shell lignin modified phenol formaldehyde wood adhesive

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Lignin modified phenol formaldehyde wood adhesives have been prepared by replacing phenol with the groundnut shell lignin (GNSL) at varying weight percentages. The optimization of weight percent incorporation of GNSL was carried out in respect to mechanical properties. It was found that a maximum of up to 50 wt.% of phenol in the phenol formaldehyde (PF) adhesive can be substituted by GNSL to obtain lignin substituted phenol formaldehyde (LSPF) adhesive with improved adhesive and shear strength in comparison with PF adhesive. The adhesive composition having 50 wt.% of phenol substituted by GNSL, termed as LSPF50 showed highest adhesive strength. LSPF50 and PF were further characterized by IR, DSC and TGA. Gel time measured and DSC showed higher rate of curing / hardening in LSPF50 than in PF. Thermogravimetric analysis (TGA) suggests C stage curing of LSPF50 adhesive at about 150/160 °C while for PF at about 160/185°C.

Keywords: Groundnut shell lignin, Lignin substituted phenol formaldehyde, Wood adhesive

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Lignocellulosic agriculture waste such as bagasse, coconut coirpith, coffeebean shell, rice husk and other products has been used in the development of adhesives. In the context of utilization of lignin from agricultural waste, groundnut shell (GNS) is one of the suitable sources of lignin because of its high availability in the country. In 2004, the production of 75 million tones of groundnut was recorded.

Lignin is being explored as a substitute of phenol in phenolic adhesive, as a coating material for structural polymers and dispersant. Sulphonated lignin was used as a reinforcing agent in rubber. It was also used as a stabilizer or antioxidant in polymeric composition. Lignin has been incorporated in thermoplastic material to increase their stability and mechanical properties. Glasser and co-workers have done extensive work on the preparation of polyurethane and other plastics from lignin. Lignin is a natural binder in wood and resembles structurally with PF resin. The chemical structure of lignin macromolecule is very complex. The structural monomeric repeat unit in lignin is 1-(p-hydroxy phenyl) propane-3-ol having a methoxy group in the ortho position of the phenolic ring. It contains both the phenolic and hydroxyl groups, which can be used as reactive sites for chemical modification. Partial replacement of phenol by lignin can be very useful in making lignin substituted phenol formaldehyde (LSPF) adhesives. Lignin can be incorporated into PF resin in three ways: (i) it can be reacted with formaldehyde to provide methylol functionalities and then added to PF resins, where lignin acts as an extender; (ii) condensing the lignin directly with phenol and formaldehyde and (iii) derivatizing lignin either with phenol or formaldehyde to enhance its reactivity towards PF resins. Substitution of phenol by lignin is expected to reduce the cost and curing time and improve the strength and water resistance. Plywood prepared from lignin substituted phenolic adhesive was found to produce lower wood failure as compared with those prepared using control PF resin. The shear strength of lignin substituted adhesive was found to be comparable or better than the standard PF adhesives.

The literature survey reveals that some research work on differently derived lignin modified wood adhesives has been done but no work on GNSL modified adhesive has been reported. The main objective of this study is to explore the possibility of replacing phenol by GNSL in resole PF wood adhesive. Keeping this in view, the effect of varying weight percent of GNSL incorporation on physico-mechanical properties of LSPF adhesives has been studied. The loading of GNSL in the PF adhesive which gave the best properties is termed as
optimized loading. The optimized LSPF and PF adhesives were further investigated for their thermal characterization.

**Experimental Procedure**

**Materials**

Phenol (Qualigen, India), formaldehyde 37% (Merck, India), sulphuric acid and methanol (S.D. Fine Chemicals, India) and sodium hydroxide (Rankem, India) were used for the experimental work. Groundnut “bold” variety was procured from M/s Samex Agency, Bulsar, Gujrat, India. Ground nut was dehulled and shell waste was used as a source of lignin. It was washed with distilled water, dried in an oven at 100±5°C for 8 h and subsequently used for delignification.

**Isolation of lignin**

Isolation of lignin from dried GNS was performed in a two-neck round-bottom flask equipped with a condenser and a thermometer. Ground nut shell (225 g) and sodium hydroxide solution (2.25 kg of 5 mol/L) were charged into the flask. Temperature was maintained at 100±1°C for 7 h. Black liquor so obtained was filtered to remove suspended pulp fibres and then was precipitated with 50% sulphuric acid solution. The precipitated lignin was washed with acidified water ($pH$ 2). A lignin cake (112.5 g) was obtained. The lignin cake was dried at 100°C for 8 h and then under vacuum at 80°C for 8 h to obtain dried lignin (56 g). The yield of lignin was found to be 25% on dry basis.

**Synthesis of adhesives**

PF and LSPF adhesives were synthesized in a four-neck round-bottom flask equipped with a stirrer, thermometer, condenser and dropping funnel. For preparation of PF, 23.28 g of phenol (0.246 moles), 37.8 g formaldehyde solution (0.456 moles), 20 g each of distilled water (1.1 moles) and methanol (0.62 moles) were charged in a flask. The mixture was heated and the temperature was maintained at 80±1°C. A solution of sodium hydroxide 1.16 g (0.029 moles) was then added and reaction was continued for 4 h.

LSPF was synthesized using the methodology described by Khan et al. The first step consists of in the preparation of lignin-phenol (LP) adduct and the second step consists of the preparation of LSPF adhesive. In the first step, 50 g of GNSL cake having 12.5 g of lignin on dry basic was transferred in a beaker and 12.5 g phenol (0.133 moles) was added to it. The mixture was mixed and stirred for an hour at 40°C to obtain a homogenous paste. In the second step, 26 g of LP adduct, 42 g of formaldehyde solution (0.518 moles), 10 g of methanol (0.31 moles) were mixed and heated at 80°C. A solution of 1.16 g of sodium hydroxide (0.029 moles) was then added and reaction was maintained at 80±1°C for 4 h. Reaction yielded LSPF adhesives. By varying the amount of phenol and GNSL as required the LSPF adhesives with 25, 35, 50 and 60 weight percent incorporation of lignin with respect to phenol were prepared. These adhesive compositions were termed as LSPF25, LSPF35, LSPF50 and LSPF60, respectively.

**Characterization of lignin and adhesives**

The GNSL, PF and LSPF adhesives were characterized by various techniques to obtain information about their chemical, physico-chemical, thermal and mechanical properties. The following techniques and instruments were used for this purpose.

The elemental analysis of GNSL was carried out using a CHN Rapid Elemental Analyzer model Heraeus 5002651.10-20 mg lignin was placed in an oxidative combustion chamber at 950°C using cerium oxide as oxidation catalyst. The FT-IR spectra of GNSL and adhesives were recorded on an FT-IR spectrophotometer model NICOLET Impact 410 using a KBr pellet containing 1 wt.% of finely ground samples. The pellets were dried in an oven at 100±5°C for 2 h. The weight percent of non-volatile content (solid content) of the adhesives were measured according to ASTM D-4426-93 method. The gel time of adhesives was measured using the standard ASTM D2471-88 method. Approximately 400 g of adhesive was placed in an open top container at 100± 1°C. At every 15 s a wooden probe was inserted perpendicularly into the surface of the reacting mass. The gelation time was determined when the reacting material no longer adhered to the end of the probe. The apparent viscosity of PF and LSPF was measured with Rotoviscometer RV-30, Haake, Germany. The adhesive samples were equilibrated to constant temperature at 25°C before recording the viscosity at constant shear (400 S⁻¹). The glass transition temperature of ($T_g$) of lignin and curing of adhesives were determined using model DSC 2910, TA Instruments, USA. The sample (8 mg) was heated at a rate of 10°C/min from ambient
temperature to 150°C under N2 atmosphere in a sealed aluminum pan. The thermal stability of lignin was investigated using same instrument in dynamic mode. The sample (8 mg) was heated at a rate of 10°C/min from ambient to 500°C in N2 atmosphere. For thermal degradation studies of resins, the instrument was used in dynamic mode and the sample (8 mg) was heated at a rate of 10°C/min from ambient temperature to 700°C in N2 atmosphere.

The method for testing the bonding strength of the adhesives has been recommended differently by Indian standard (IS) and American standard for testing of materials (ASTM). Here, both the standard methods for testing the bonding/adhesive strength of the adhesives have been used. IS: 851-1978 describes the method for testing the adhesive strength of a close contact joint of the samples. The teakwood specimens with moisture content of 7 wt.% were cut into size of 115×25×3.15 mm. The adhesive was applied on two specimens. Two adherents were joined together by applying the adhesive on 25×125 mm area. The glued samples were then pressed in a clamp under a load of 50 kg. The samples were kept in an oven at 125±2°C for 2 h. The samples were conditioned at ambient temperature (27±2°C) and moisture content (60±5%) until constant weight was observed. The specimens were tested for bond strength on an Instron testing machine at a crosshead speed of 50 mm min\(^{-1}\). The load taken by the samples were recorded and average bond strength of six test specimens was determined. The shear strength was measured by tension loading of adhesives as per ASTM D 2339-94 A. 3-Ply laminate of moisture content 7 wt.% (on dry basis) was used for specimens preparation of size 300×100×3 mm. The adhesive was applied on the whole surface of one side of the adherents. The two panels were glued and assembled to each other, keeping the grain in parallel. The glued samples were pressed in a compression molding machine at 120°C at a pressure of 40 kg cm\(^{-2}\). The panel was cured for 6 min and then cooled. After conditioning at ambient temperature (27±2°C) and 60±5% humidity until constant weight, the panels were cut into 82.6×25.4 mm specimens. A groove of 3 mm depth was engraved on both sides of adherents and the area between the groove was kept 25×25 mm. The specimens were tested for shear strength using Instron machine at a crosshead speed of 3 mm min\(^{-1}\). The load taken by the samples were recorded and average shear strength of six test specimens was determined.

### Results and Discussion

**Characterization of GNSL, PF and LSPF**

The percent yield of GNSL was found to be 25 wt.%. Lignin extracted from groundnut shell was characterized for hydroxyl value, inherent viscosity (\(\eta_i\)), glass transition temperature (\(T_g\)) and elemental analysis using the standard procedure. A hydroxyl value of 217 mg, inherent viscosity of 0.6 dl/g, glass transition temperature of 108°C and carbon, hydrogen and oxygen wt.% fractions of 46.4, 4.8 and 48.8 were found within the range of the reported values of these parameters of some other lignin extracted from different sources\(^1,2\).

Figure 1 shows the FT-IR spectra of GNSL, PF and LSPF50 adhesives. The IR bands are assigned as follows: 3365 cm\(^{-1}\), OH stretching vibration; 2910 cm\(^{-1}\), asymmetric CH\(_2\) vibration; 1725 cm\(^{-1}\), C=O stretching of aldehyde/ketone groups; 1620 and 1500 cm\(^{-1}\), C=C stretching vibration in benzene ring; 1260 cm\(^{-1}\), C-O stretching vibration of secondary alcohol; and 1040 and 925 cm\(^{-1}\), in plane and out of plane deformation vibration of syringyl groups of lignin. These bands match well with the reported values of characteristic vibrations in other lignins\(^21\). The IR spectra of PF and LSPF50 adhesives are shown in Fig. 1. The IR bands for various groups of LSPF adhesive were identified as follows: 3400 cm\(^{-1}\), OH stretching vibrations; 2923 cm\(^{-1}\), CH\(_2\) asymmetric stretching peak; 2842 cm\(^{-1}\), CH\(_2\) symmetric vibrations; 1600 and 1500 cm\(^{-1}\), C=C stretching vibration in benzene ring; 1458 cm\(^{-1}\), CH deformation mode in CH\(_3\) group (appearance of this band in LSPF indicates the presence of – CH\(_2\) bridge in the system); 1230 cm\(^{-1}\),

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Fig. 1—IR spectrum of GNSL, LSPF50 and PF adhesive
C-O stretching in syringyl phenolic group \(^{23}\); 1130 cm\(^{-1}\), stretching vibration of ether linkages; 1050 cm\(^{-1}\), C-O stretching of methylol groups in the system. Saad \textit{et al.}\(^{23}\) have identified 1725 cm\(^{-1}\) peak of GNSL spectra as lignin bond (Fig. 1). It appears that ketonic group undergoes enol formation in LSPF and causes the band to shift to a lower frequency. The bands in IR spectra of PF adhesives were assigned as follows: 2927 cm\(^{-1}\), CH\(_2\) asymmetric stretching peak; 2842 cm\(^{-1}\), CH\(_2\) symmetric vibrations; 1591 and 1481 cm\(^{-1}\), C=C stretching vibration in benzene ring; 1208 cm\(^{-1}\), C-O stretching in phenolic group; 1140 cm\(^{-1}\), stretching vibration of ether linkages; and 1030 cm\(^{-1}\), C-O stretching of methylol groups in the system. IR analysis shows similarity in structures of LSPF and PF adhesives.

**Physico-mechanical analysis of adhesives**

The mechanical properties of LSPF and PF were studied for adhesive and shear strengths. Figure 2 shows the effect of GNSL wt.% incorporation on the adhesive and shear strengths of PF adhesive. The PF adhesive showed adhesive and shear strengths equal to 11.16 and 15.4 kg cm\(^{-2}\), respectively. In LSPF25 the adhesive strength was found to increase by 24.3% and the shear strength by 25% over PF adhesive. LSPF35 showed small increase in adhesive and shear strengths as compared with LSPF25. However, LSPF50 in which 50 wt.% of phenol was substituted by GNSL showed an increase in adhesive and shear strengths of 38.5 and 42.2%, respectively. LSPF60 showed the adhesive and shear strengths equal to 15 and 21 kg cm\(^{-2}\), respectively. The later adhesive showed a small decrease in shear strength from LSPF50 while the adhesive strength remained same as that of LSPF50. It is, thus, observed that the incorporation of GNSL in PF adhesive increases the bonding strength of PF adhesive up to 50 wt.% of phenol. Thus, GNSL which is a product from an agricultural waste can be successfully incorporated into PF adhesive replacing not only phenol but also increasing its strength.

It is reported that bonding strength of the adhesive depends upon crosslink density. The increase in adhesive and shear strength of LSPF adhesive is attributed to higher extent of polycondensation and crosslink formation due to large availability of phenolic moieties in lignin molecules. Above results also show that at 50 wt.% substitution of phenol by GNSL polycondensation and crosslink formation becomes maximum and further substitution of phenol by GNSL does not contribute to polycondensation and crosslink formation. Hence, 50 wt.% substitution of phenol by GNSL is optimal for making LSPF adhesive.

The physical properties of PF and LSPF adhesives are summarized in Table 1. Nonvolatile content of LSPF adhesives with different weight percent loadings of lignin is comparable with PF. This shows the similarity of the chemical nature of the two adhesives which has also been found by IR analysis. Gel time of LSPF was found to decrease with increasing loading of lignin in PF adhesive. Gel time for LSPF50 was found to be half of that of PF adhesive. The decrease in gel time indicates that crosslinking rate noticeably increases with increased loading of GNSL in PF adhesive due to higher availability of phenolic moiety and methylol groups and consequently higher rate of polycondensation. The lower gel time, therefore, shows the lower time of the conversion of reactants into thermoset through crosslink formation. Viscosity of LSPF was found to increase with increased amount of GNSL in PF adhesive. LSPF50 has 2.25 higher viscosity than PF. The higher viscosity of LSPF composition than PF results from higher molar mass and bulkier GNSL molecule.

![Fig. 2—Mechanical strength of PF and LSPF adhesives](image)

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<th>Physico-chemical properties of adhesives</th>
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<td>Non-volatile content (%)</td>
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DSC thermograms of PF and LSPF50 adhesives are shown in Fig. 3. In both adhesive systems, an endotherm is obtained which is correlated to curing or hardening of the adhesives\(^2\). The onset temperature (\(T_o\)), peak temperature (\(T_p\)), and \(\Delta T = (T_p - T_o)\), noted from endothermic curve of LSPF50 and PF are 85, 111 and 25°C, and 85, 126 and 41°C, respectively. The end temperature of endothermic curves, \(T_f\) for LSPF50 and PF are observed at 138 and 160°C, respectively. The \(\Delta T\) denotes the curing rate\(^2\). Christiansen and Gollob\(^2\) have also reported that the endothermic curves in the DSC thermograms of PF and LSPF adhesive indicate curing or hardening of adhesives. Since, during curing/hardening of the PF/LSPF adhesives, methylene bridges and ether linkages are formed between phenolic moiety with the evolution of water and formaldehyde, that entails weight loss. TGA curves of PF and LSPF50 (Fig. 4) show weight loss in the range of endothermic curves conforming the occurrence of polycondensation and crosslink formation in this temperature range on DSC thermogram (Fig. 3).

It is also observed that in case of LSPF50, \(\Delta T\) is 25°C while it is 41°C in case of PF. The lower value of \(\Delta T\) for LSPF50 shows higher rate of curing as compared to PF adhesive. The above results are also correlated by gel time studies, which have shown that rate of polycondensation, and crosslink formation in LSPF50 is higher than that in PF. The gel time in case of LSPF50 is 50% that of PF, while \(\Delta T\) value in case of LSPF50 is 62% that of PF. The rates of polycondensation and crosslink formation indicate that the methods for LSPF50 and PF are comparable though the experimental conditions in the two methods are significantly different from each other.

TGA thermogram of PF adhesive (Fig. 4) shows distinctly two weight loss events, one between 85 to 274°C and the other between 274 and 622°C. The first event entails a weight loss of 11.2 wt.%, while the second event entails a weight loss of 24.78%. It has been observed, that, in case of resole the first hardening occurs below 160°C when rubbery hard mass is formed which is called resitol while above 160°C a hard, infusible dark coloured mass is formed\(^2\). The two hardening processes are called ‘B’ stage and ‘C’ stage curing, respectively. As already evident from the DSC thermogram of PF that endothermic curve spans between 85 and 160°C, however between this temperature range a weight loss of 4.18 g is recorded which can be correlated to the liberation of water and formaldehyde. It can, thus, be inferred that ‘B’ stage curing can be accomplished below 160°C and more preferably at 126°C which is the peak temperature in the PF endotherm. Since, a second thermal event starts from 274°C onwards involving a weight loss of about 24.78%, this can be correlated to the decomposition events in the PF adhesives. For ‘C’ stage curing a temperature, which is away from the onset temperature of thermal degradation, can be chosen. For example, 185°C, which is above 160°C and involves a weight loss of 7.5% due to evolution of water and formaldehyde but involves no weight loss due to chemical degradation, can be chosen for ‘C’ stage curing.

In case of LSPF50 the TGA curves shows a weight loss of 5.31 g between 85 and 138°C, which coincides with the endothermic curves representing curing/hardening of LSPF50. The ‘B’ stage curing/hardening of the adhesive can be done at peak temperature of the endotherm, that is, 110°C. Since, lignin is a large molecule curing/hardening starts at a lower
temperature than in case of PF. Similar to the case of PF, in this case also weight loss continues with the heating. A distinct degradation event appears between 160 and 292°C, which involves a weight loss of 16%. A second degradation event runs between 292 and 700°C involving a weight loss of 21.83%. This weight loss is caused by the chemical degradation of LSPF adhesive which turns it into char. It, thus, appears that for ‘C’ stage curing the temperature where this adhesive sets into hard infusible mass but does not involve chemical degradation, 160°C can be chosen. The weight loss at the former temperature is 7 wt.% which is due to the liberation of water consequent to further crosslink formation and quinine methide formation and its further polymerization. By comparing the weight loss at different temperatures, it can be inferred that PF adhesive is thermally more stable than LSPF50.

Conclusions
(i) Phenol (50 wt.%) can be replaced in PF adhesive by GNSL extracted from alkali delignification of groundnut shell. The resulting LSPF adhesive shows higher adhesive and shear strength (bonding strength). Further, phenol replacement by GNSL in PF adhesive up to 60 wt.% can be done as the resulting LSPF adhesive shows comparable mechanical strength with LSPF50.
(ii) LSPF adhesive shows shorter gel time, which indicates higher rate of polyecondensation and crosslink formation in these adhesives.
(iii) The decreased value of $\Delta T$ (from DSC thermogram) being much lower in LSPF50 than PF also shows higher rate of polyecondensation, crosslink formation and hardening as compared to PF.
(iv) Thermal stability of PF is found better than LSPF resin.
(v) GNSL being a product from agrowastes can be used to substitute phenol upto 50% in PF adhesive with improved mechanical strength than the PF adhesive.

References