

## Synthesis of Lignin Based Phenolic Resin and its Utilization in the Exterior Grade Plywood

<sup>1</sup>TASLEEM AKHTAR\*, <sup>2</sup>GHOSIA LUTFULLAH AND <sup>3</sup>RUBINA NAZLI

<sup>1</sup>PMRC Research Centre, Khyber Medical College, Peshawar, Pakistan.

<sup>2</sup>Centre of Biotechnology, University of Peshawar, Peshawar, Pakistan.

<sup>3</sup>Department of Biochemistry, Khyber Girls Medical College, Peshawar, Pakistan.

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**Summary:** This paper reports on plywood glued by adhesives based on lignin-phenol-formaldehyde resins. Lignosulfonate was isolated from sodium based spent sulfite liquor, a waste product of the paper mills in Pakistan, where different grasses are being used as raw material for pulping. Lignin was characterized by using ultraviolet and infrared spectroscopy. Resin was synthesized by polycondensation of lignosulfonate with phenol and formaldehyde in alkali medium under reflux. Various properties of the adhesive measured, indicate that phenol can be replaced by lignosulfonate up to 70 % without affecting the quality of the glue. Plywood made with these resins was tested in the dry and wet states [cold water resistance, warm water resistance, boiling water resistance and mycological]. The glue shear load of the plywood, in all states met the requirements imposed by Pak. Std. 871, 1970. Wood failure of plywood was compared with commercial standard (CS) 3545 and the results found were equally good.

### Introduction

The major adhesive resin worldwide used in the manufacture of plywood is phenol-formaldehyde resole (PF) resin. The raw material for this kind of adhesive is derived from petroleum oil. Because of rising prices of crude oil and the scarcity of petroleum products, their replacement by natural resource-based raw material has become a necessity. The main focus of scientists all over the world is to carry out research on non-petrochemical phenolic compounds, such as lignin and tannins [1, 2].

Lignin is a natural polyphenol, consisting phenylpropane units. The supply of lignin is large, being the major by product of pulping processes for paper making; they constitute 24-33 % of the woody substance in softwoods and 16-24 % in hardwoods [3]. During sulfite pulping of wood the lignin is sulfonated [4] and is usually obtained as a by product in the residual pulping liquor commonly referred as "spent sulfite liquor" (SSL), consisting mainly of lignosulfonate (LS) [5].

In most of the paper industries in the world, wood is used as the raw material for pulping but in Pakistan due to shortage of wood, all the paper mills utilize grassy materials, such as bagasse (*Saccharum officinarum*), kaigrass (*Saccharum spontarum*) and wheat straws (*Triticum vulgare*). The lignin from

these grassy materials is composed of guaiacyl-syringyl units where syringyl has been found to be the dominant unit [6, 7]. In Pakistan, the black liquor (BL) from the paper mills is discharged into the rivers causing serious health problems to human and aquatic lives. In other developed countries, BL is used for various purposes; including lignin based wood adhesive where its methylene bridge is utilized in phenol-formaldehyde [8-12] and urea formaldehyde [13-15] types of resins. Replacement of phenol by lignin in phenol-formaldehyde resin has an economical effect and reduces the pollution caused by draining black liquor into rivers and streams.

Since SSL obtained from wood pulp has already been used as a binder for the plywood industry [16, 17] it is desirable to investigate the potential uses of the BL from grassy pulp.

In the present work, the possibility of replacing phenol in PF resin with lignin was explored. The changes in resin properties like polymerization time, reaction temperature, solid content, glue curing time, pH, pot life, density and viscosity with increasing the content of lignin in the PF resin, were optimized and used as a binder for plywood.

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\*To whom all correspondence should be addressed.

## Results and Discussion

Properties of different glues prepared are shown in Table-1. Density and viscosity of the glue increases by gradual replacement of phenol with lignosulfonate, which is evident from the corresponding increase of total solids. Similar results are reported by Nada *et al.* [10, 18], where lignosulfonate obtained from SSL based on rice straws as pulping material was used to prepare PF-lignosulfonate adhesives. They observed that in the adduct stage; the resins are becoming more viscous by increasing the amount of lignosulfonate. This increase in the viscosity may be attributed to enhance cross linking between phenol, lignosulfonate and formaldehyde. As the lignin based phenolic resins achieve higher viscosities more quickly than the pure phenol-formaldehyde resin, the reflux time had to be reduced with the increasing amount of lignosulfonate in the adhesive. This is probably due to the huge size of lignin and initial charge of polymeric fraction in the lignin based phenolic adhesive [19]. Pot life of the adhesive also increased with the increasing amounts of the lignosulfonate in the resin (Table-1). This rise in pot life is most probably due to highly cross linked complex structure of PF-lignosulfonate adhesive. The active sites if any are hindered by the bulky groups and no further condensations are possible or activation energy required for further condensations is not achieved at room temperature. Therefore, rate of further condensation is very slow resulting in high pot life. However, pH of the glue and glue curing time at 150 °C remained more or less constant for the adhesives prepared from different combinations of phenol-formaldehyde and lingo-sulfonate. This is in accordance with the findings of Muller *et al.* [19] which showed that activation energies and cure rates determined by differential scanning calorimetry (DSC) showed no difference between adhesives and high lignin contents and had no inhibitory effects on adhesive cure. Khan *et al.* [20] found that up to 50 wt. % of phenol could be replaced by lignin to give an lignin phenol-formaldehyde adhesive with better bonding strength when compared to the pure PF resin.

In the present study these resins were used in the preparation of plywood and were tested both in the dry and wet states (cold water resistance (CWR), warm water resistance (WWR), boiling water resistance (BWR) and mycological).

Table-1: Properties of PF-LS adhesive at different concentration of PF and lignosulfonate.

Adhesive (%)		pH	Total solids (%)	Pot life (days)	Density (g/cm <sup>3</sup> )	Viscosity (cp) at 30 °C
LS	PF					
0	100	10.7	25.65	21	1.880	880
10	90	9.78	52.27	32	1.192	917
20	80	9.88	58.07	45	1.200	1003
30	70	9.78	59.26	63	1.206	1080
40	60	9.57	60.20	90	1.210	1155
50	50	9.55	62.90	128	1.224	1210
70	30	9.50	65.00	147	1.232	1322

Table-2 shows mean shear failing load of Eucalyptus at different composition of PF-LS resins in both dry and wet state. The failing load decreases with the increasing amount of lignosulfonate in the resin. No significant difference was observed in the failing load of the plywood in dry and wet states at various ratios of phenol-formaldehyde to lignosulfonate, where the two forms are almost overlapping each other. This show, strength properties are not affected by water under various wet conditions, suggesting that these resins are water resistant. The present work indicates the lowest glue failing load of 217 Kg (WWR) even at a glue composition 70:30 of lignosulfonate to phenol-formaldehyde, while according to PS 871:1970, the average dry glue failing load in respect of BWR grade is 135 Kg. It was also observed that the failing load constantly decreasing in all the states except CWR where it increases from 10 to 20 % addition LS and then decreases with the increasing amount of lignosulfonate (up to 40 %) in the resin. Further increase of lignosulfonate in the resin produced no worsening effects and the failing load remained approximately constant, up to 70 % substitution of phenol by lignosulfonate in the resin.

The effect of different glue compositions on the average wood failure of the plywood is represented in Table-2. A clear difference was observed in the wood failure between dry and wet states. The same difference was maintained in the dry and wet states of pure PF indicating that the PF-LS resins are affected by water to same degree as pure PF. It was observed that in both states wood failure increases with the increase of lignosulfonate (10-20 %) in the resin, then it decreases up to 50 % addition, while further addition of lignosulfonate (up to 70 %) showed a constant behavior. BWR test for pure phenol-formaldehyde indicated a low value of wood failure (40 %), but the wood failure increased by the addition of 10 % lignosulfonate and remained constant by further addition of LS.

Table-2: Mean shear failing load of Eucalyptus at different composition of PF-LS resins in both dry &amp; wet state.

PF-LS Adhesive		Dry		CWR 24 hours		WWR 3 hours		BWR 8 hours		Mycological 2 weeks	
PF (%)	LS (%)	Failing load (Kg)	W.F (%)	Failing load (Kg)	W.F (%)	Failing load (Kg)	W.F (%)	Failing load (Kg)	W.F (%)	Failing load (Kg)	W.F (%)
100	0	488	82	485	43	475	42	420	28	445	44
90	10	353	90	315	56	360	46	375	47	380	48
80	20	305	92	320	44	322	50	305	47	310	50
70	30	280	67	270	34	283	38	290	44	310	34
60	40	258	66	250	37	255	38	263	35	275	50
50	50	260	53	290	40	225	28	275	36	250	30
30	70	250	54	235	42	215	22	262	42	250	30

Note:

According to PS 871; 1970, the average dry glue failing load in respect of BWR grade is 135Kg.

According to CS 3547, average wood failure is 50 % for a failing load of 114Kg.

Wood failure values obtained from present study were compared with commercial standard [21] CS-3547 at various glue compositions of phenol-formaldehyde and lignosulfonate (Table-3). The result obtained are better than those of the commercial standard even at a glue composition 70:30 of lignosulfonate to phenol-formaldehyde.

Table-3: Comparison of the commercial standard with wood failure to the corresponding failing load of the plywood.

Failing load (Kg)	Av. wood failure (%)
114	50
114-159	30
> 159	15
249*	53

\*Result from this study at a glue composition 70:30 of lignosulfonate to phenol-formaldehyde in dry state.

It is clear from the results that lignosulfonate modified resins are capable of producing water resistant bonds. This implies that lignosulfonate is actually participating in cross linking reactions to make it a part of the cured adhesive net-work.

### Experimental

Black liquor was collected from the Adamjee Paper and Board Mills, Nowshera, NWFP, Pakistan, where sodium based sulfite pulping process is being used. They use bagasse, kaigrass and wheat straws as pulp material. Lignosulfonate was isolated from black liquor by Willstatter's method [22] and characterized by using ultraviolet and infrared spectroscopy.

For the synthesis of PF-LS resin a fixed ratio of 100:110:5 phenol, formaldehyde and sodium hydroxide (by weight) was used. The reaction

temperature was optimized at 105 °C for a period of one and half hour. Similar glues were prepared by gradual replacement of phenol with lignosulfonate, keeping the amount of formaldehyde and sodium hydroxide same. The reflux period had to be decreased with the increasing amount of lignosulfonate in the adhesive due to rapid rise in viscosity, while the other reaction conditions were kept same. Upto 70 % of phenol was successfully substituted with lignosulfonate. A pure phenol-formaldehyde resin was also prepared for comparison purposes. Various properties measured, included pH of the glue, the density, viscosity, total solids and glue curing time at 150 °C. Pot life of the glue was also noted.

The amount of glue required in the manufacturing of plywood was calculated on the basis of total solid of the glue spread of the veneers. For 100 grams of glue (solid contents 52-65 %) the following formulation was used;

Glue	= 82 gms
Paraformaldehyde	= 10 gms
Walnut shell powder	= 4 gms
Sodium hydroxide (50 % soln.)	= 2 gms
Wheat flour	= 2 gms

Plywood was prepared from *Eucalyptus camaldulensis* having a density of 0.676 g/cm. Three plies of rotary cut veneers of dimension 50 cm, 55 cm, 0.159 cm and moisture contents of 9 % were used. A single glue line was applied on both sides of the core layer and the veneers were assembled in plywood construction with grain of the face at right angle to the core layer. To all the panels' preparations with different glues an initial glue setting time of 20 minutes was given. Plywood loose panels were

pressed under a pressure of 14 kg/cm<sup>2</sup> at 150 for 12 mins.

After conditioning for one week at 65 % relative humidity (Rh) and temperature 23 ± 2; shear specimens were prepared according to the American Society of Testing Materials (ASTM) [23]. The following tests were performed according to PS. 871:1970; (plywood for general purposes).

1. Glue shear load in dry state (at 65 % Rh, 23 ± 2).
2. Glue shear load in wet state
  - (a) Cold water resistance (CWR): soaking in water for 24 hrs at room temperature.
  - (b) Warm water resistance (WWR): soaking in water for 3 hrs at 70 °C.
  - (c) Boiling water resistance (BWR): boiling in water for 8 hrs.
3. Test for resistance to micro-organism (Mycological testing).

The test specimens were submerged for a period of two weeks at room temperature in saw dust (poplar) moistens with a sufficient amount of an aqueous solution of sugar cane.

The average shear load of the specimens at failure and the average wood failure were calculated. Twenty shear specimens were used for each test per plywood prepared from different glues.

### Conclusion

It has been concluded from this study that although the glue shear load of plywood decreases with increasing amount of lignosulfonate (up to 40 %) in the resin, there was no significant difference in the glue shear loads of the dry and wet specimens. This indicated that the plywood produced from the various glue combinations of PF and lingo-sulfonate are water resistant. 70 % of phenol could be successfully replaced by LS and even more substitution might still produce plywood of international standard (*i.e.* British standard).

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