Black Liquor Substituted Phenolic Adhesives for Fire Retardant Particle Board

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ABSTRACT

Black liquor obtained from rice husk was utilized as a partial substitute for phenol in the preparation of phenolic adhesive for particle board. A few fire retardant compositions studied to achieve fire retardancy were found quite effective in improving physical characteristics as well as fire performance of the product.

KEY WORDS: Black liquor, phenol formaldehyde-black liquor resin, particle board, modulus of rupture, water absorption.

INTRODUCTION

Black liquor is a by-product of paper industry. The paper mills largely use bamboo and hard woods for pulp and paper production. During pulp and paper-making processes, only 50% of the ligno-cellulosic material is converted into the final product while the rest 50% being present in the black liquor. Presently, black liquor is either thrown away or used as a fuel. The drainage of black liquor is a waste of valuable organic matter containing mainly lignin. If this by-product is put to some use it would undoubtedly improve the economic viability of paper mills.

Phenolic resins are largely used for making various wood based products. Lignin being phenolic in nature can replace phenol in the production of cheaper resin. Isolated lignins have been used in the preparation of a large number of resins and resinous compositions offering possibilities as a substitute for phenol in the development of phenol substituted resin. Many investigators have evaluated the use of lignin as adhesive for wood bonding[1–8]. Still there are a number of problems associated with utilising lignins as adhesives. Lignin preparations can be quite heterogeneous depending upon wood species and pulping process used. Lignins have low reactivity with formaldehyde when compared with phenol[4]. Methylolation, demethylolation and ultrafiltration separation were studied in order to increase lignin reactivity[5, 9]. The different modified lignins were tested in preparation of lignin phenol formaldehyde resin binders[5]. The methods used for developing such resins is not economical and suitable for industrial use as the pot life of the resin is very short.

Black liquor which is a rich source of lignin can replace phenol in the production of resin. This process will be more economical and easier than involving precipitation of lignin from black liquor, since the step for liberating lignin from black liquor has been completely eliminated. This would result in saving a lot of time and chemicals used in its precipitation etc. Another area which has not been explored is the utilisation of lignin and lignin products in the production of fire retardant materials. If highly combustible cellulosic materials are rendered fire retardant huge losses of life and property can be minimized.

The present communication deals with the utilization of black liquor in its readily available form i.e. obtained after digestion of pulping material for making adhesives, which may be used for the production of fire retardant particle board.

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EXPERIMENTAL

Material

All the reagent used in this investigation were of laboratory reagent grade. Rice husk and wood chips were procured from the local market.

Preparation of Black Liquor

Black liquor was prepared by pulping rice husk in an autoclave at appropriate conditions of temperature and pressure. The conditions were as:

Alkali 12–14%; bath ratio 1:6; temperature 165 ± 5°C; time 4 hrs; pressure 1.8 kg/cm^2.

Black liquor was collected after filtering and kept in air-tight container. It was analysed for various physico-chemical properties following standard methods. Solid contents, density at 20°C, pH and lignin concentrations were found to be 14.86%, 1.06 g/mL, 9.5–10.0 and 10.92% respectively. The elemental analysis showed carbon, hydrogen and oxygen as 42.5%, 06.4% and 51.1%. The methoxyl, hydroxyl, pentosan phenolic and carbonyl functional groups were analyzed as 8.40, 6.60, 2.50, 2.16 and 0.11 percent.

Preparation of Resin from Black Liquor

Black liquor phenol formaldehyde (BLPF) resins were formulated, replacing phenol by black liquor of rice husk. For comparing purposes a phenol-formaldehyde (PF) resin was also prepared using only phenol and formaldehyde.

Resins were prepared by reacting phenol with 37% formalin in the presence of an alkaline catalyst. Phenol was replaced with varying amount of black liquor. During preparation pH was adjusted to 9.5 in a reactor for 40–50 minutes at 90°C. The resin so prepared was allowed to cool down and stored in an airtight container. Solid content and density of different resins were determined.

Preparation of Particle Board

The manufacturing process of particle board consisted of mixing dried wood chips with resin in a container. The varying amounts of resin was mixed in weighed quantity of wood chips. The resin blended particles were spread in a mould and pressed in a hot press at various temperatures applying 18–20 kg/cm^2 pressure for different time. The specimens were conditioned at 65 ± 5% R.H. and 27 ± 2°C temperature for one week. Effect of temperature, duration of pressing and resin content on the properties of particle board were determined.

To achieve fire retardancy in particle boards a few fire retardants listed in Table 2 were studied. Fire retardants were mixed at the rate of 15–18% loading of dry wood chips in the resin. Particle boards were prepared as usual and evaluated for their burning, physical and mechanical properties.

Evaluation of Performance of the Product

A few characteristics such as density, moisture content, modulus of rupture (M.O.R.) and water absorption were evaluated according to Indian standards IS : 2380 and 3087 methods[10, 11]. Effect of fire retardants on M.O.R. and water absorption was also determined.

Fire performance was evaluated by exposing the specimen to a severe condition. For exposure, a Bunsen burner of 9 mm inner dia with LPG as a fuel was used. Specimens of particle board (8 × 150 × 305 mm) were hanged vertically with the help of hooks. The gas burner of about 50 mm flame height was placed in such a way that the base of the flame was 25 mm below the middle of the lower edge of the specimen. The flame was applied for different time up to 30 minutes. After that, it was withdrawn and then afterflame time, afterglow time and weight loss were measured.

RESULTS AND DISCUSSION

The analysis of lignin extracted from rice husk black liquor shows the presence of hydroxyl group, both phenolic and alcoholic indicating the possible reaction site. The analysis of black liquor shows that the solid contents were 14.86% consisting of dissolved and suspended solids. Lignin was found 10.92% in the rice husk. The pH 9.5–10.0 of black liquor indicates that it was having unused alkali. Table 1 shows the characteristics of adhesives in which phenol was replaced with black liquor in

TABLE. 1. Formulations and Characteristics of BLPF Resins

Phenol Replaced (%)	Black Liquor (g)	Phenol (g)	Formalin (g)	Density g/cm^3
10	20	180	360	1.10
20	30	120	270	1.10
30	54	126	324	1.08
40	126	189	567	1.07
50	170	170	612	1.05
60	180	120	540	1.05
70	210	90	540	1.05
80	160	40	360	1.03
90	135	15	270	1.02
100	175	00	315	1.02
00	00	150	270	1.08

varying proportions. It was observed that as the amount of black liquor increased in the resin preparation, the solid contents of the resin goes on decreasing (Fig. 1). It was experimentally established that as the solid contents of the resin decreases, higher temperature and longer duration are required to obtain maximum strength of the product.

It is found that resin content influences the properties of particle boards. With increase in the resin content the value of modulus of rupture (M.O.R.) increases and water absorption characteristic of the product decreases (Fig. 2). It is noted that the boards prepared using below 8% resin content on solid weight basis do not pass the requirements specified in standards.

It is observed from the data obtained on the effect of temperature and time on setting of the resin evaluated by determining M.O.R. that adhesive developed by replacing phenol by black liquor require more time and higher temperature in comparison of pure phenol formaldehyde resin (Fig. 3).

It is noted from the data of M.O.R. that the product developed with adhesive up to 60% replacesment of phenol with black liquor meet the requirement of Indian Standards (IS : 2380 and 3087). At this, replacement product did not pass the requirement specified in the standards for water absorption. It is also observed that addition of fire retardants based on phosphate salt and urea increase the modulus of rupture and decrease the water absorption characteristics of the particle board. The product developed with the addition of fire retardants meet the requirement of water absorption even with 60% replacement of phenol (Table 2). In this, the crosslinking of resin and fire retardants to cellulose may be expected to take place. However, the exact mechanism is being investigated.

From the burning test data it is noted that melamine, borax and urea alone are not effective in reducing the burning characteristics of the product while phosphate salt was found little effective. On the other hand, the combination of phosphate salt and urea was found more effective in comparison

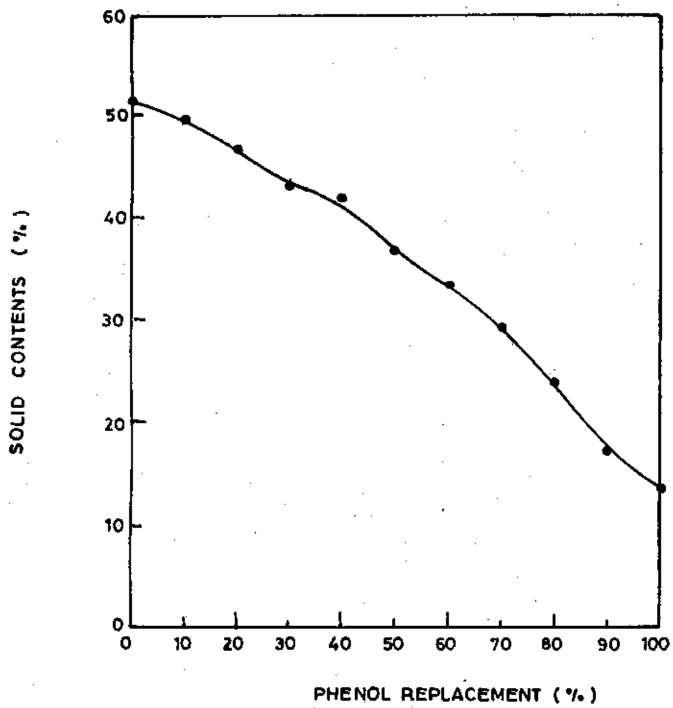

Fig. 1. Effect of phenol replacement on solid contents of BLPF resin.

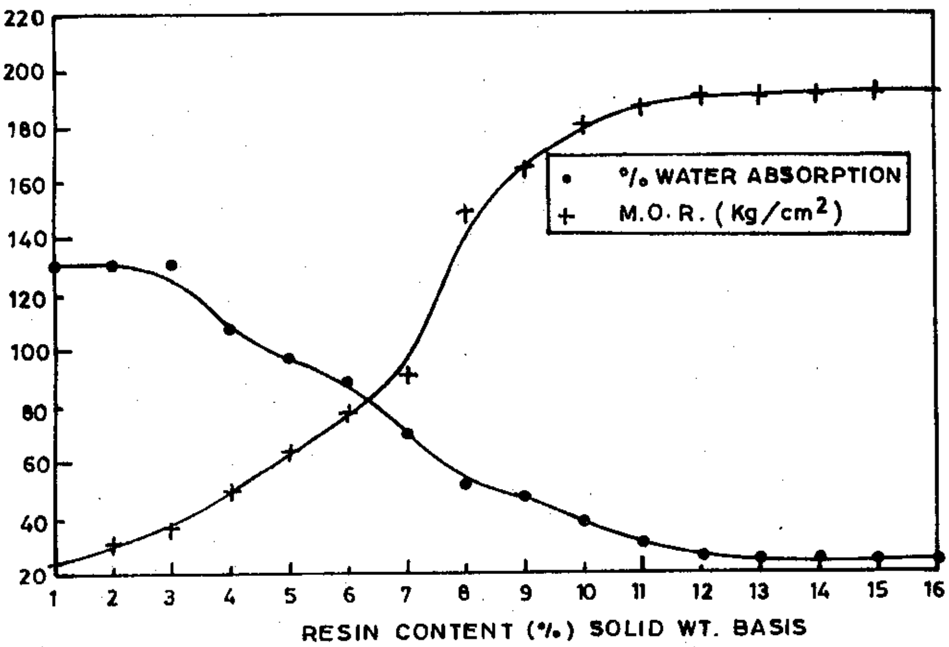

Fig. 2. Effect of BLPF resin content on M.O.R. and water absorption.

to the combination of phosphate salt-borax and phosphate salt-melamine (Table 3). It is also noted that the combination of phosphate salt-urea was more effective with BLPF resin. The specimens of particle boards were burnt completely within 1.5 minutes with flame and afterglow combustion while specimens having fire retardants did not ignite under the similar conditions of exposure even up to 30 minutes (Table 4). The function of phosphorus-containing fire retardants appears to alter the course of decomposition of the cellulosic materials so that lower amounts of flammable volatiles and larger quantities of char are formed thereby reducing the flammable characteristics of cellulosic materials[12–14]

CONCLUSION

Wood based panel products are very much used in buildings for diverse applications. These materials are highly combustible and pose great fire hazard. The resins used for making these products are costly. Black liquor is a by-product of paper industry posing disposal and environmental pollu-

TABLE. 2. Characteristics of Particle Board

Resin Used	Type of Board	Density (kg/m^3)	Water Absorption (%) After 24 h.	M.O.R. (kg/cm^2)
PF	Flat Pressed Single Layer (FPS)	660–832	050.50	162.00
BLPF-20	-do-	-do-	048.60	170.00
BLPF-40	-do-	-do-	042.80	170.00
BLPF-60	-do-	-do-	074.50	134.20
BLPF-80	-do-	-do-	112.70	032.00
BLPF-100	-do-	-do-	131.20	003.90
PF+FR Additives (FRA)	-do-	-do-	046.00	164.00
BLPF-20 + FRA	-do-	-do-	043.50	167.20
BLPF-40 + FRA	-do-	-do-	037.75	193.60
BLPF-60 + FRA	-do-	-do-	067.90	171.70
BLPF-80 + FRA	-do-	-do-	103.20	041.20
BLPF-100 + FRA	-do-	-do-	129.50	005.20
Requirement As Per IS: 3087	-do-	500–900	< 070.00	> 090.00

BLPF-20, 40 ....indicates 20%, 40%, ...phenol replaced.

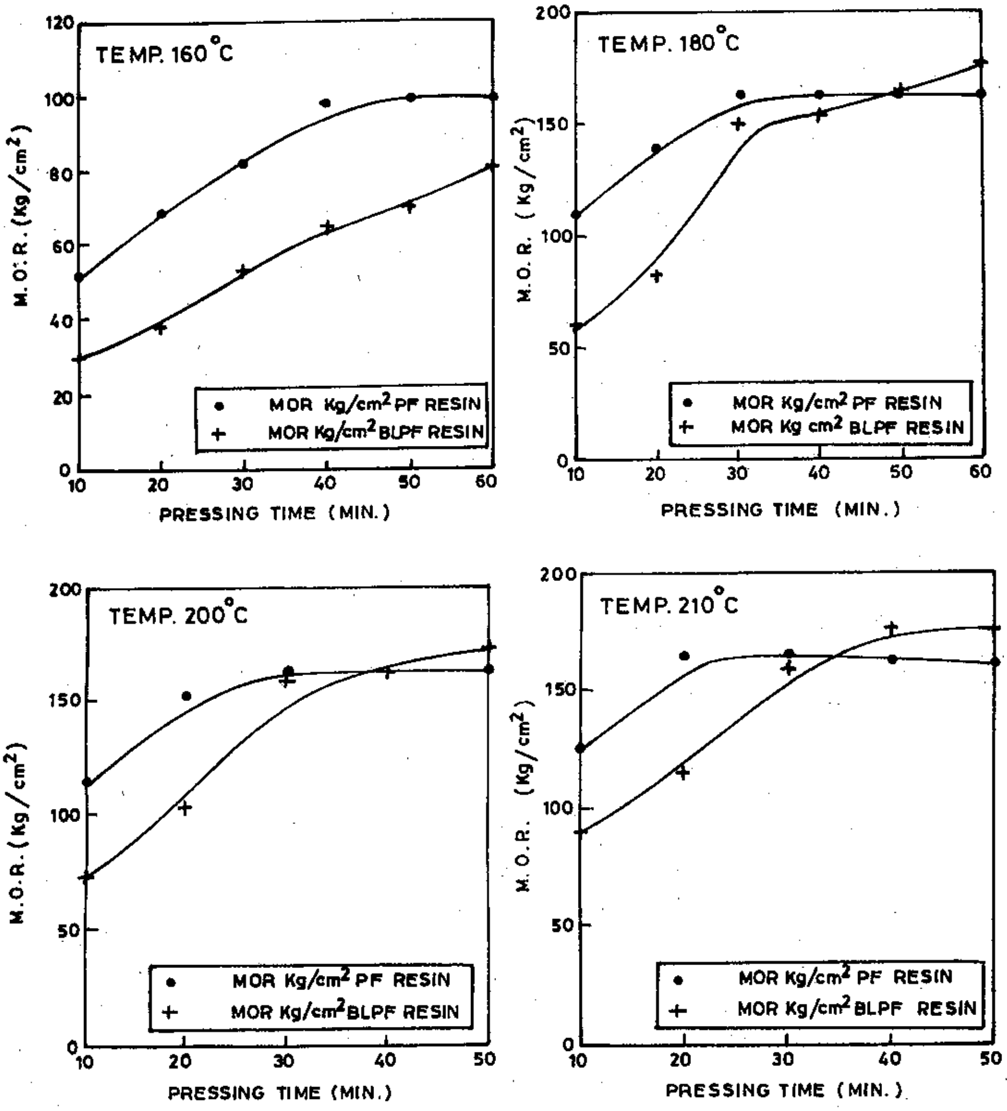

Fig. 3. Effect of temperature and time on M.O.R. of particle boards.

tion problems can profitably be utilized to obtain cheaper resins. It is concluded that materials developed using rice husk black liquor based adhesive satisfied the requirement specified in the standards. The combinations of fire retardants studied were found effective in reducing the burning characteristics of the product. It is also concluded that combination of phosphate salt and urea is also effective in increasing the modulus of rupture and decreasing water absorption characteristics of the product. Thus, adhesives based on phenol replacement up to 60% by rice husk black liquor may be utilized in developing cheaper materials having improved fire performance and physical characteristics.

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TABLE. 3. Effect of Fire Retardants on Fire Performance

Fire retardant	Time of exposure (min.)	Afterflame time (sec.)	Afterglow time (sec.)	Wt. loss (g)	Remarks
Phosphate Salt	5	8	34	26.2	Self-extinguished
Melamine	5	24	Contd.	Burnt	Completely burnt by afterglow combustion
Borax	5	15	82	34.4	Burnt completely
Urea	5	26	Contd.	Burnt	—do—
Phosphate Salt +Borax (1 : 2, w/w)	5	0	7	13.8	Self-extinguished
Phosphate Salt +Urea (1 : 2.2, w/w)	5	0	0	0.72	—do—
Phosphate Salt + melamine (1 : 1.5, w/w)	5	0	5	9.80	—do—
Blank	5	38	Contd.	Burnt	Burnt completely

TABLE. 4. Fire Performance of the Board With Phosphate Salt and Urea

Particle Board with	Initial Wt. of Speci-men (g)	Time of exposure (min.)	Afterflame time (sec)	Afterglow time (sec)	Wt. loss (gms)	Remarks
PF + FRA	54.8	05	00	000	0.69	Self-extinguished
-do-	55.4	10	00	000	3.20	-do-
-do-	54.5	30	06	600	12.40	Afterglow combustion observed after that self-extinguished.
BLPF-40 +FRA	55.2	05	00	000	0.52	Self-extinguished
	54.7	10	00	000	2.40	-do-
	55.6	30	04	282	9.80	Afterglow observed after that self-extinguished
PF Resin	55.2	05	82	Cont.	Burnt	Completely burnt with afterglow combustion within 1.5 minutes.
BLPF Resin	54.7	05	67	Cont.	Burnt	-do-

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