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Alkali Treated Kraft Lignin as a Component in Flakeboard Resins[1]

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Summary

Southern pine kraft lignin was reacted with NaOH (15 and 20% based on dry lignin) at 170, 200, and 250°C for 30 and 60 min. Sweetgum flakeboards bonded with phenolic resins containing 50% hydroxymethylated lignin prepared from some of the alkali treated lignins were compared with boards bonded with a neat PF resin. Results indicate that boards bonded with lignin-containing resins have a satisfactory bending strength. Boards bonded with resins prepared by reacting lignins with phenol and formaldehyde have better internal bond strength and durability than those bonded with lignin-extended resins. However, there is no evident advantage in using alkali treated lignin in the manufacture of phenol-lignin-formaldehyde resins for flakeboard application.

NMR spectral analyses indicated that the phenolic hydroxyl content of alkali treated lignins increases with increasing severity of reaction condition. The increase in the phenolic hydroxyl content, however, is accompanied by a decrease in free C5 positions in the guaiacyl moieties due to the formation of GC5–C5G and GC5–CH_2–C5G bonds during the reaction. Because of condensation of C5 positions, the degree of hydroxymethylation of alkali treated lignins with formaldehyde also decreases with increasing severity of the reaction.

Introduction

A primary objective of lignin utilization research has been to use industrial lignins as binders or to incorporate them into phenolic wood adhesives for panel products. A thorough discussion of the development of lignin-based wood adhesives can be found in Nimz (1983).

Roffael and Rauch (1971, 1972, 1973) successfully used spent sulfite liquor as part of the exterior particleboard binder by mixing it with phenol-formaldehyde resins. The reactivity of industrial lignins is much lower than that of phenolic resins because of their low phenolic hydroxyl content and high ring substitution and steric hindrance (Lin 1983). For these reasons, only a limited amount of industrial lignin can be used as a direct replacement for phenol in the formulation of phenolic adhesives without losing adhesive strength (Falkehag 1975; Nimz 1983). However, a greater replacement can be achieved by using modified lignins (Holderby *et al.* 1967; Ludwig and Stout 1972; Enkvist 1973; Forss and Fuhrmann 1976; Dolenko and Clarke 1978; Muller *et al.* 1984). Of all modification treatments, those that increase the reactivity of lignin such as demethylation, phenolation, and methylolation seem the most effective. In a recent review, Glasser (1989) showed examples of lignin modification to achieve a high degree of lignin incorporation into different types of thermosetting materials.

Hydrolysis of lignin, either in alkaline or acidic medium, degrades lignin molecules and thus can generate new phenolic hydroxyl groups. Although a substantial amount of simple phenols can be produced by acid hydrolysis of lignin (Lundquist 1970), acid hydrolysis of lignin is usually carried out in nonaqueous medium, and the hydrolysed lignin has to be separated from the organic solvent before it can be utilized. In addition, Muller *et al.* (1984) found that acid-hydrolyzed lignin was incompatible with the nor-

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mal process of phenolic resin synthesis. Under proper conditions, alkaline hydrolysis of industrial lignins yield reactive degradation products useful for condensation reactions of phenolic resins (Enkvist *et al.* 1962; Clark and Green 1968; Enkvist 1975). Another advantage of using alkaline hydrolysis to modify industrial lignins is that the hydrolyzed products can be directly used in phenolic resin synthesis.

Earlier interests in studying alkaline hydrolysis of lignin emphasized production of monomeric phenolics. In the present study, an attempt was made to modify polymeric lignin molecules of a technical kraft lignin by various alkaline conditions. Some of the alkaline-hydrolyzed lignins were selected to replace part of the phenol in phenol-formaldehyde resin synthesis, and the lignin-containing phenolic resins were evaluated in the application of flakeboard manufacture.

Materials and Methods

Alkaline hydrolysis

A southern pine kraft lignin, Westvaco Indulin-AT in the powder form, was used. Kraft lignin 30% aqueous solution containing 15 or 20% NaOH based on dry lignin were hydrolyzed in a Parr pressure reactor with presence of air at three maximum temperatures (170, 200, and 250°C) for two reaction times (30 and 60 min). On the average, it took 20 min to raise the reaction from room temperature at 170°C, 23 min to 200°C, and 30 min to 250°C. At the end of the reaction, the mixture was cooled down to room temperature in 20 min by running cold water through the cooling loop in the reactor. A total of 12 hydrolysis reactions (Table 1) were performed.

Preparation of lignin samples

Hydrolyzed lignin products were acidified with 0.5 N H_2SO_4 to pH 4, and the precipitated solids were collected by centrifugation. The solid mass was washed 3 times with distilled water and dried in a vacuum oven at 45°C overnight.

Hydroxymethylation of isolated lignin samples was carried out in the following manner. The lignin sample was dissolved in NaOH solution, and formaldehyde solution (37%) at a molar ratio of 1 lignin (based on a molecular weight of 180) to 1.6 formaldehyde was poured into the lignin solution. The mixture was adjusted with NaOH to pH 12 and refluxed at 70°C for 4 hr with constant stirring. At the end of the reaction, the mixture was acidified with 0.5 N H_2SO_4 to pH 4, and the precipitate was centrifuged off. After washing 3 times with distilled water, the hydroxymethylated lignin solid was dried in a vacuum oven at 45°C overnight.

Acetylation of lignin samples was performed by following a procedure described by Mansson (1983). The lignin sample (200 mg) was acetylated with a mixture of 1 ml acetic anhydride and 1 ml pyridine for 15 hr. Then, 1 ml of methanol and 8 ml of dichloromethane were added, and the mixture was allowed to react for an additional 30 min. The mixture was washed with HCl (2M) and dried with Na_2SO_4, and the solvents were evaporated by using a rotary evaporator.

No effort was made to determine yields for acid precipitation, hydroxymethylation, and acetylation of hydrolyzed lignins.

Gel permeation chromatography

The relative molecular weight distribution of alkali treated lignins was compared. Acid precipitated lignins were dissolved in 0.1 N NaOH, and 50 μl of the solution containing 0.5 mg of lignin was chromatographed on a Sephadex G-100-120 column (1 cm × 100 cm) using 0.1 N NaOH as solvent with a flow rate of about 20 ml/hr. The eluent was monitored with a spectrophotometer at 280 nm.

NMR spectroscopy

^{13}C (75 MHz) and ^{1}H (300 MHz) NMR spectra of lignin samples were obtained on a Bruker WM-300 WB spectrometer. ^{1}H NMR spectra of acetylated lignin samples (30 mg in 0.5 ml deuterated chloroform) were recorded at room temperature. For each spectrum, 32 scans were collected using 75° pulse width, 2.05 sec acquisition time, and 5 sec relaxation delay. The chloroform resonance signal was set to 7.25 ppm as the chemical shift reference. To quantify various ^{1}H NMR signals in lignin samples, an external standard of TSP [2,2,3,3-tetradeutero-3-(methylsilyl)-propionic acid, sodium salt] dissolved in D_2O and placed in a coaxial tube was used. The ^{13}C NMR spectra were obtained at probe temperature of 95°C by using a sample concentration of 600 mg of lignin sample in 3 ml of deuterated dimethylsulfoxide (DMSO). Spectra were obtained by using 45° pulse width, 0.41 sec acquisition time, and 1 sec relaxation delay. A total of 9000 scans were collected for each spectrum. All ^{13}C chemical shifts were referenced to the resonance signal of DMSO set to 39.5 ppm. The ^{13}C NMR spectra were recorded without NOE, and no quantitative analysis of these spectra was performed.

Resin formulation

The unhydrolyzed kraft lignin (Indulin-AT) and hydrolyzed lignins obtained from reaction 10 and 11 (Table 1) were selected to prepare lignin-containing resins. Two types of lignin-containing resins were prepared. In the first type, 250 g of the selected lignin sample was first hydroxymethylated as described earlier. At the end of the hydroxymethylation reaction, the lignin mixture was cooled to about 50°C, and an amount of a commercial PF resin (Borden PB-83) containing 250 g of solids was slowly added with vigorous mixing for about 10 min before being cooled to room temperature. Finally, an additional amount of NaOH was added so that the viscosity of these blended resins was controlled below 500 cps for suitable spraying. To prepare the second type of resin, 250 g of the selected lignin sample also was first hydroxymethylated. At the end of the hydroxymethylation of lignin, 250 g of phenol (Kodak, practical), together with 345 g of 37% formaldehyde solution, 22.5 g of NaOH, and 273 g of water, was added to the mixture. The mixture was allowed to react between 70 and 75°C for 1 hr. Ten grams more of NaOH was added, and the temperature was rapidly raised to 95°C. As soon as the viscosity of the mixture reached about 500 cps at 25°C as determined by a Brookfield-LVF viscometer, 10 more grams of NaOH was added, and the mixture was rapidly cooled to room temperature.

Flakeboard manufacture and testing

The lignin-containing resins were evaluated by comparing with Borden PB-83 liquid PF resin. Resins were applied at a rate of 7% resin solids based on the oven dry weight of 0.01-mm-thick sweetgum lathe flakes. Mats were hand-felted in a 35.6 cm × 40.6 cm forming box. Boards with a thickness of 1.27 cm (0.5 inch) and a target density of 0.7 g/cm^3 were consolidated in the following manner: 175°C platen temperature, 1 min to closing, 5 min at the maximum pressure, 10 min total press time. The strength properties of flakeboards were evaluated according to procedures described in ASTM D1037 (1974). For accelerated aging tests, specimens were boiled in water for 2 hr, and values of linear expansion, percentage thickness swell, and wet modulus of rupture were measured immediately after boiling.

Results and Discussion

Alkaline hydrolysis of lignin

Within the range of NaOH usage investigated, the highest workable concentration of Indulin-AT aqueous solution was about 30%. Beyond this concentration, the lignin solution became very viscous at room temperature. Table 1 shows changes in pH and viscosity of lignin solutions subjected to various hydrolysis conditions, and Figure 1 shows the relative molecular distribution of selected hydrolyzed lignins.

With the exeption of reaction 6, the pH of the hydrolyzed lignins decreased, and the viscosity and weight loss increased, with increasing severity of the reaction condition. The exceptionally low viscosity of reaction 6 product (15% NaOH, 250°C) is due to partial charring of the lignin, resulting in the production of insoluble products. GPC study (Fig. 1) indicated that at the 15% NaOH usage level, the high-molecular-weight fraction of the lignin increased with increasing reaction temperature. At the 20% NaOH usage level, however, the high-molecular-weight fraction decreased with increasing reaction temperature. From this GPC study, it seems that increase in viscosity with increasing severity of hydrolysis condition is mainly due to decrease in pH during the reaction.

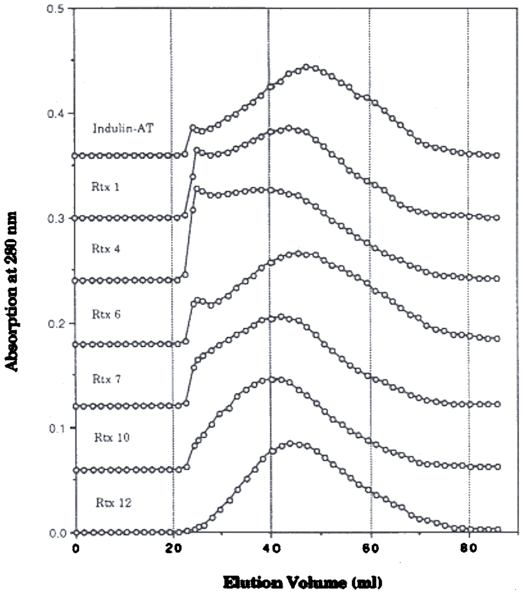

Fig. 1. Gel permeation chromatography of kraft lignin and alkali treated lignins on Sephadex G-100-120 column with 0.1 N NaOH as solvent.

Table 1. Conditions of lignin hydrolysis reactions and properties of hydrolyzed lignins

Reaction	NaOH[1] usage (%)	Max. temp. (°C)	Time at max. temp. (min.)	pH		Viscosity[2] (cps)		Solid content (%)		Solid loss (%)
				Init.	End	Init.	End	Init.	End	
	15	170	60	12.2	11.7	23	131	29.3	29.3	0
	15	170	120	12.2	11.6	23	238	29.2	28.9	1.0
3	15	200	30	12.2	11.7	23	162	28.7	28.8	0
4	15	200	60	12.2	11.5	22.5	475	28.8	28.0	2.78
5	15	250	30	12.2	10.7	22.5	gel	28.8	28.5	1.04
6[3]	15	250	60	12.2	10.7	22.5	307	29.1	27.4	4.80
	20	170	60	13.5	12.9	20	19	29.5	29.2	1.0
8	20	170	120	13.5	12.7	20	19	29.8	29.0	2.68
9	20	200	30	13.5	12.5	20	16	29.2	28.6	2.05
10	20	200	60	13.5	12.3	20	20	29.5	28.3	4.10
11	20	250	30	13.5	11.5	20	84	29.9	27.7	7.40
12	20	250	60	13.5	11.5	20	5200	29.5	27.5	6.78

[1] Based on the dry weight of lignin.
[2] Determined with a Brookfield-LVF viscometer at 25°C.
[3] Charring of lignin occured.

Table 2. Comparison of relative integrals of various NMR signals in the acetylated lignins (AL) and acetylated hydroxymethylated lignins (AML) with TSP as an external standard

Lignin samples		$-OCH_3$ 4.4–3.2 ppm	ϕ-Acetate 2.90–2.18 ppm	R-Acetate 2.18–1.40 ppm	Increase of R-OAc/OCH_3
Rtx 0	AL	18.2 (1.0)[1]	9.6 (0.53)	15.3 (0.84)	
INDULIN-AT	AML	18.2 (1.0)	10.0 (0.55)	20.2 (1.11)	(0.27)
Rtx 1 15% NaOH	AL	18.2 (1.0)	10.0 (0.59)	15.8 (0.87)	
170°C 60 min.	AML	18.3 (1.0)	10.8 (0.59)	20.1 (1.10)	(0.23)
Rtx 4 15% NaOH	AL	18.5 (1.0)	14.0 (0.76)	15.6 (0.84)	
200°C 60 min.	AML	18.4 (1.0)	13.9 (0.76)	18.9 (1.03)	(0.19)
Rtx 6 15% NaOH	AL	16.3 (1.0)	16.1 (0.99)	14.7 (0.90)	
250°C 60 min.	AML	not measured because of low solubility			
Rtx 7 20% NaOH	AL	18.2 (1.0)	11.1 (0.61)	15.5 (0.85)	
170°C 60 min.	AML	18.0 (1.0)	11.0 (0.60)	19.7 (1.09)	(0.24)
Rtx 10 20% NaOH	AL	18.2 (1.0)	13.5 (0.74)	15.5 (0.85)	
200°C 60 min.	AML	18.0 (1.0)	13.3 (0.74)	18.9 (1.05)	(0.20)
Rtx 11 20% NaOH	AL	17.0 (1.0)	15.4 (0.91)	13.9 (0.82)	
250°C 30 min.	AML	17.1 (1.0)	15.1 (0.88)	16.4 (0.96)	(0.14)
Rtx 12 20% NaOH	AL	15.5 (1.0)	15.9 (1.03)	12.7 (0.82)	
250°C 60 min.	AML	not measured because of low solubility			

[1] Values in parentheses are relative integrals with the value of $-OCH_3$ as an internal standard in each lignin sample.

^{1}H NMR spectra

^{1}H NMR spectra of acetylated Indulin-AT and some of hydroyzed lignins are given in Figure 2. In the ^{1}H NMR spectra, signals at about 3.9, 2.3, and 2.0 ppm correspond to methoxyl group, aryl acetate, and aliphatic acetate, respectively. Integration of these signals by using TSP as an external standard are shown in Table 2. Because hydrolyzed products of reactions 6 and 12 had a very low $CDCl_3$ solubility after hydroxymethylation followed by acetylation, satisfactory spectra could not be obtained from these samples. Although the ^{1}H NMR spectra were not highly resolved. Table 2 provides a close estimation of various hydrolysis reactions. For example, Chen *et al.* (1985) found that 0.3 equivalent of $HO-CH_2$ group/$-OCH_3$ was introduced into the kraft lignin by the hydroxymethylation reaction, and the corresponding value obtained in this present study is 0.27.

Table 2 shows that the methoxyl contents of lignin samples hydrolyzed at 170 and 200°C are nearly the same as that of the unhydrolyzed kraft lignin. This result indicates that little demethylation occurred when the kraft lignin was hydrolyzed with 15 and 20% NaOH at or below 200°C. Some demethylation, however, was observed when the kraft lignin was hydrolyzed at 250°C. The phenolic hydroxyl content of the hydrolyzed products, on the other hand, increased with increasing severity of hydrolysis conditions, indicating an increase in the cleavage of phenolic ether bonds with increasing reaction temperature. Therefore, the results indicate that aromatic methoxyl

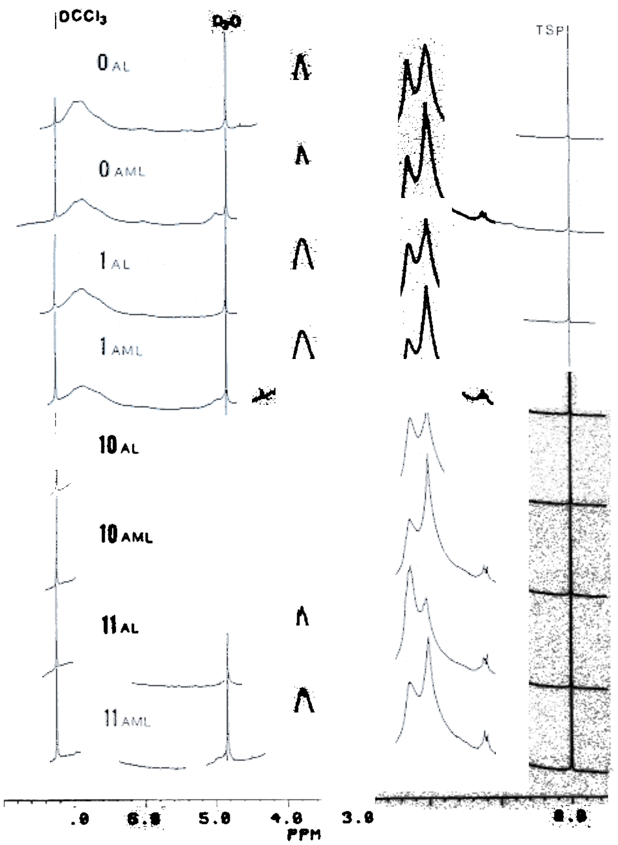

Fig. 2. ^1H NMR spectra of some representative acetylated lignin samples. Numbers and subscripts denote different lignins as listed in Table 2.

groups are more resistant to alkaline hydrolysis than other types of aryl-alkyl ethers, i.e., β-aryl ethers.

Table 2 also shows that the aliphatic hydroxyl content of lignin samples hydrolyzed at 170 and 200 °C is about the same as that of the unhydrolyzed kraft lignin. This implies that very little or no change in aliphatic hydroxyl content occurred during alkaline hydrolysis at or below 200 °C. Comparison of the aliphatic acetate content of acetylated samples with those of hydroxymethylated and acetylated samples reveals that amount of CH_2OH groups introduced into lignin molecules decreased with increasing severity of hydrolysis condition. Because there is very little change in the hydroxyl content of the side chain during alkaline hydrolysis below 200 °C, reduction in the degree of hydroxymethylation of hydrolyzed lignins must be due to reduction in the available free C5 position in the guaiacyl moieties.

^{13}C NMR spectra

Some of the ^{13}C NMR spectra of lignin samples are shown in Figure 3. The solubility of the hydroxymethylated lignin obtained from reaction 12 was so low in DMSO that satisfactory spectrum of this sample could not be obtained. Chemical shift assignments listed in Table 3 were selected for analyses. Assignments of these chemical shift signals are based on the study of Kringstad and Mörck (1983).

Table 3. ^{13}C chemical shifts and resonance assignment (Kringstad and Mörck 1983) selected for studying the effect of alkaline hydrolysis of lignin

	Chemical shifts (ppm)	Assignment
1	142	C4 with substituent on C5
2	127.7	C5, substituted
3	126	C5 in GC5–C5G biphenyls
4	116	C5 with various side chain structures
5	85.5	Cβ, β-aryl ethers
6	72	Cα, β-aryl ethers
7	61	γ*CH_2OH
8	58.5	GC5–*CH_2OH
9	55.8	OCH_3
10	29	CH_2 in GC5–CH_2–C5G

Kringstad and Mörck (1983) showed that the isolated spruce lignin from fully pulped spent liquor contained minor amounts of β-aryl ether structures. These β-aryl ether structures, shown by signals at about 85.5 and 72 ppm in Figure 3, are found to be further reduced by alkaline hydrolysis of the kraft lignin. Cleavage of

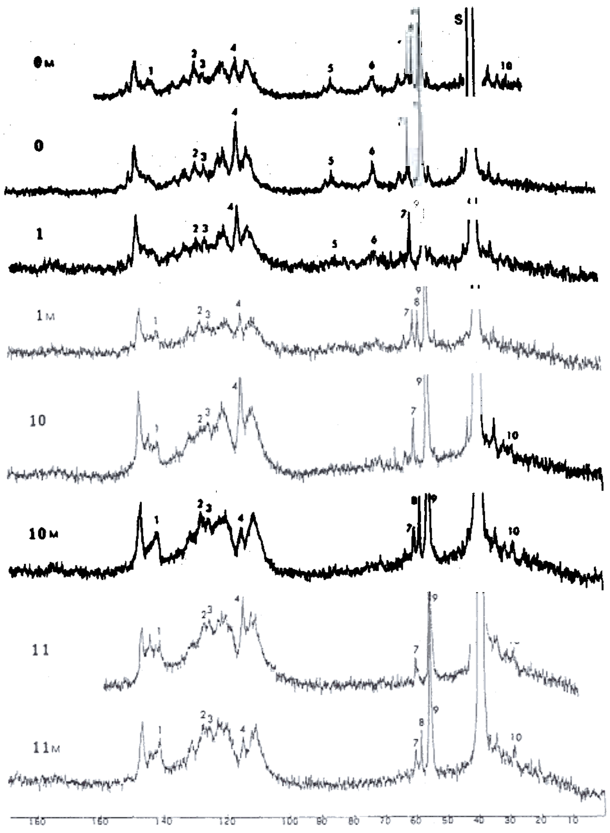

Fig. 3. ^{13}C NMR spectra of some representative lignin samples. Numbers denote conditions of alkaline hydrolysis as listed in Table 1, and subscript M denotes hydroxymethylated lignin.

β-aryl ether bonds is responsible for the increase in the phenolic hydroxyl content of hydrolyzed lignins as shown earlier in the ^{1}H NMR study.

The increase in the phenolic hydroxyl content, however, presents no advantages in increasing the reactivity of hydrolyzed lignins with formaldehyde owing to condensation reaction at guaiacyl C5 positions. Evidences of guaiacyl C5 condensation are given by changes in signal intensities at 142 and 127.7 ppm. The intensity of these two signals increased with increasing severity of alkaline hydrolysis of the kraft lignin, indicating an increasing degree of substitution at the GC5 position. Hydrolysis of the kraft lignin also caused a parallel increase in the intensity of signals at 126 and 29 ppm, suggesting that GC5−C5G and GC5−CH_2−C5G are two main types of guaiacyl C5 substitutions. Because the increase in the signal intensity at 29 ppm is accompanied by a decrease at 60 ppm, the CH_2 group in GC5−CH_2−C5G may have come from γCH_2OH in the side chain. This type of condensation reaction has been identified as a major condensation reaction during alkaline pulping (Gierer *et al.* 1976).

Hydroxymethylation of lignins with formaldehyde in alkaline solution resulted in a strong signal at about 59 ppm. The signal at 59 ppm, assigned to $HOCH_2$−C5G (Kringstad and Mörck 1983), provides the evidence of the introduction of hydroxymethyl groups at GC5 positions. Hydroxymethylation of lignin also increased signal intensities at 142 and 127.7 ppm. The increase in the intensity at these two signals provides a further evidence of the introduction of hydroxymethyl groups at GC5 positions. In addition, hydroxymethylation of lignin also reduced the signal intensity at 116 ppm, which has been assigned to free GC5 with various side chain structures (Kringstad and Mörck 1983). The fact that signal at 116 ppm was only reduced but not totally eliminated indicates that the hydroxymethylation of lignins is not quantitative. Marton *et al.* (1966) and Chen *et al.* (1985) also found that of 65 GC5/100 phenyl units in pine kraft lignin (Mansson 1983), only about 39 and 30 hydroxymethyl groups, respectively, could be introduced onto the GC5 positions by the hydroxymethylation reaction.

Resin formulation and flakeboard properties

Physical properties of two types of lignin-containing resins, both with a 50% phenol replacement, are given in Table 4. Resins of the first type (A0, A10, and A11) are lignin-extended PF resins because they were

Table 4. Properties of resins and sweetgum flakeboards bonded with lignin-containing phenolic resins

		Resin properties			Flakeboard properties[1]					
					Dry Strength			2−hr boiling tests		
Resins	Lignin	pH	Viscosity (cps)	% Solid contents	MOR (Kpa)	MOE (Mpa)	IB (Kpa)	Wet MOR (Kpa)	TS (%)	LE (%)
Borden PB-83		11.5	300	45.0	23,994	3,661	689	10,231	37.	0.14
			Lignin-extended resins							
A0	Indulin AT	11.8	375	38.9	22,415	3,247	345	8,177	54.4	0.26
A 10	Hydrolyzed Rtx 10	12.2	375	37.0	23,497	3,419	407	9,721	42.7	0.24
A 11	Hydrolyzed Rtx 11	12.2	490	38.2	23,552	3,475	476	11,804	39.6	0.20
			Phenol-lignin-formaldehyde resins							
B 0	Indulin AT	11.7	380	46.	22,615	3,447	503	9,653	44.3	0.23
B 10	Hydrolyzed Rtx 10	11.8	485	44.6	21,677	3,420	489	9,011	38.7	0.25
B 11	Hydrolyzed Rtx 11	11.5	490	42.4	24,483	3,433	476	9,859	41.3	0.19

[1] Each value is the average of 3 boards tested; resin solid content = 7%, based on dry wood; board density = 0.7 g/cm^3

prepared by blending equal amounts of a commercial PF resin and hydroxymethylated lignins. The second type resins (B0, B10, and B11), prepared by reacting equal amounts of lignin and phenol with formaldehyde, can be considered as lignin-phenol copolymeric resins.

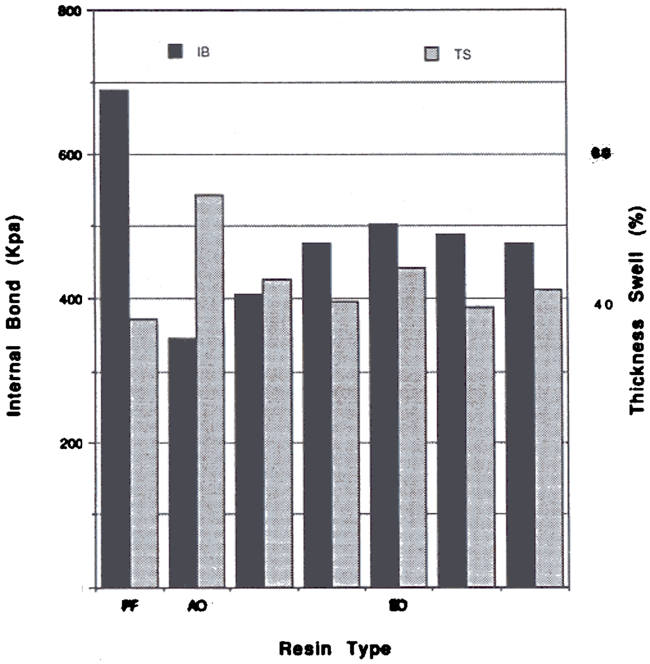

Fig. 4. Comparison of internal bond strength and thickness swell of sweetgum flakeboards bonded with PF resin and different lignin-containing phenolic resins.

Properties of sweetgum flakeboards bonded with a commercial PF resin and with lignin-containing resins also are given in Table 4. Flakeboards bonded with different lignin-containing resins and with the neat PF resin have the same level of bending strength (MOR) and stiffness (MOE). This result is to be expected because beyond a certain level of bonding efficiency, the dry bending strength is largely controlled by the flake geometry. Examination of the internal bond strength (Fig. 4), on the other hand, reveals that the phenol-lignin-formaldehyde resins performed superior to the lignin-extended PF resins. On the average, boards bonded with the phenol-lignin-formaldehyde resins also have better durability properties, especially thickness swell (Fig. 4), than those bonded with the lignin-extended PF resins. When the 3 lignin-extended PF resins are compared, there seems an advantage in using hydrolyzed and hydroxymethylated lignins as extenders. This advantage, however, was not observed when the hydrolyzed lignins were used in the synthesis of phenol-lignin-formaldehyde resins.

Conclusions

NMR studies indicated that, under the conditions used, alkaline hydrolysis failed to increase the reactivity of kraft lignin with formaldehyde. Although alkaline hydrolysis increased the phenolic hydroxyl content of kraft lignin, the increase in phenolic hydroxyl content was accompanied by an unfavorable reduction in free guaiacyl C5 positions due to the formation of GC5−C5G and GC5−CH_2−C5G linkages. Formation of GC5−C5G and GC5−CH_2−C5G linkages increased, and degree of hydroxymethylation of kraft lignin with formaldehyde decreased, with increasing severity of alkaline hydrolysis reaction.

Sweetgum flakeboards bonded with lignin-based resins prepared at the 50% phenol replacement level showed a satisfactory bending strength. Boards bonded with phenol-lignin-formaldehyde resins had better internal bond strength and durability properties than those bonded with lignin-extended PF resins. There is some advantage in using alkaline-hydrolyzed lignin as a PF resin extender, but this advantage was not observed in the synthesis of phenol-lignin-formaldehyde resins.

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