

# Modified Lignosulfonate as Adhesive

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## SYNOPSIS

Oxidized lignosulfonate (LS-OB) displays a high crosslinking during thermal condensation. When LS-OB was used as a partial substitute of urea-formaldehyde (UF) in wood adhesive, a positive effect on the curing of resin could be observed. With 30–40% substitution, no detriment in strength properties of particleboard was observed. Polycondensation of lignin and UF could occur between methylol groups in UF resin and hydroxyl and carbonyl groups in lignin, through ether bonds and methylene bridges. A high surface activity of LS-OB would reduce the surface tension of binder solution and facilitate its distribution on wood particles, improving consequently the strength properties of particleboard. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

For decades, scientists all over the world have searched for possible methods to promote the utilization of lignin in the field of engineering material, while lignin has been traditionally considered as a no-commercial-value by-product from chemical pulp mills. It is worthwhile to notice that studies have been made to use lignosulfonate contained in spent sulfite liquor (SSL) as a wood adhesive.<sup>1–3</sup> However, all of the methods reported in the literature involved the application of high pressing temperature or long pressing time when SSL was used as an adhesive in the productions of particleboards or waferboards. From the viewpoint of industry, any process requiring a high pressing temperature or long pressing time is neither economical nor practical, and the advantage of using SSL as a binder in the production would thus be offset. Therefore, more studies are needed to alleviate this drawback and to transform lignosulfonate into a useful material through a method that can be implemented in industry.

It has been reported in our previous work<sup>4,5</sup> that, during oxidation of lignosulfonate with oxygen, significant changes could be found in functional groups (i.e., hydroxyl, carboxyl, and carbonyl), as well as in the molecular weight distribution. These changes

rendered the oxidized lignosulfonate (LS-OB) to display a higher reactivity than the unoxidized one during the subsequent thermal reaction that induced self-condensation and resulted in a water-insoluble substance. The oxidized lignosulfonate could hence be expected to exhibit also a high reactivity toward urea-formaldehyde (UF) resin if it is used to substitute a part of the UF in the adhesive formulation for wood panels.

The objective of the present study was to investigate the possible linkages, revealed by IR spectra, between lignosulfonate and UF resin through a thermal reaction, so as to elucidate the condensation mechanism. Furthermore, the application of the oxidized lignosulfonate to the particleboard manufacturing will be presented.

## EXPERIMENTAL

### Materials

The lignosulfonate used was a commercial product of calcium base (Lignosol B, Daishowa Chemicals, Quebec, Canada). It was oxidized following the method described previously.<sup>5</sup> Oxidation was carried out by introducing oxygen (under a partial pressure of 2.5 atm) into a 5% aqueous solution of lignosulfonate at 150°C for a predetermined duration. Solutions of oxidized lignosulfonate (LS-OB) were adjusted to pH = 5.0 with either NaOH or NH<sub>4</sub>OH,

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and assigned hereafter as LS-ONa and LS-ONH<sub>4</sub>, respectively. These solutions were then concentrated to about 40–50% solid content at 70°C under vacuum.

Urea-formaldehyde (UF) resin, in form of latex, was provided by Borden Co. (C364-144; 65% solid) and was used as received. Wood particles of a suitable grade for the face layer of particleboards were collected from Levesque Plywood Ltd. (Ontario), which contained 70% spruce and 30% jack pine.

### Sample for IR Measurement

Two series of samples were prepared: For the first series, UF resin was mixed with the oxidized lignin (oxidation for 120 min) in different proportions so that LS-ONa (or LS-ONH<sub>4</sub>) constituted 0, 20, 30, and 40% of mixture solids. NH<sub>4</sub>Cl was added as the catalyst in a quantity equal to 0.75% of liquid UF resin. After drying at 105°C, the samples were crushed into powder and hot-pressed under a pressure of 2.9 MPa and at 180°C for 3.5 min in a special model (1.6 mm in thickness). Then the hot-pressed piece was crushed again into powders and mixed with KBr to prepare the pellets for infrared measurement (Perkin-Elmer IR Spectrophotometer, Model 283B). The second series had the same proportions between UF and LS-ONa (or LS-ONH<sub>4</sub>) as in the first one, but no NH<sub>4</sub>Cl was added. Prior to mixing with UF, the pH of LS-OB solutions was adjusted to 9.0 with NaOH (or NH<sub>4</sub>OH) to avoid chemical reactions. The mixtures were then spread uniformly on KBr pellets and dried in a desiccator at room temperature.

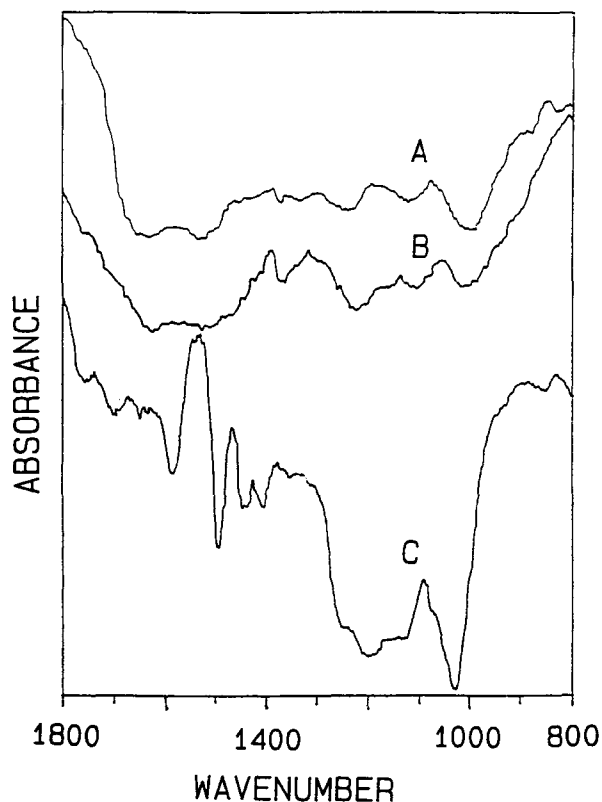
### Particleboard

Adhesive solutions were prepared by mixing UF resin with LS-OB in desired proportions, and NH<sub>4</sub>Cl was added as catalyst (1% based on UF resin). The adhesive charge used in this study was 12%, based on the oven-dry wood particles. The adhesive solution was sprayed onto the wood particles in a rotating drum. After well mixed, wood particles were hot-pressed between two aluminum plates with a laboratory oil-hydraulic press (Duke Corporation) to a thickness of three-eighth in. Hot-press was carried out at 180°C, 450 psi (3.1 MPa) for 4 min. The internal bonding strength and thickness swelling of the particleboard were measured according to the Canadian standard methods "Standard Test Method for Mat-formed Wood Particleboard (CAN3-O188.0-M)."

## RESULTS AND DISCUSSION

Though the curing mechanism of UF resin is very complicated, it has been well accepted that the formation of UF resin involves two main reactions.<sup>6,7</sup> The first one is the addition reaction where formaldehyde reacts with urea to form a so-called methylol compound, an alcohol group (C—OH) on urea. The most prevalent of these compounds in UF resin is dimethylol urea (DMU). The second is a condensation reaction where the methylol groups react with formaldehyde, urea, or another methylol group to form longer chains that make up the tridimensional matrix of the cured resin. It may be considered that two methylol end groups react to form either an ether linkage or a methylene bridge between urea molecules. During the condensation reaction, water and formaldehyde may be regenerated as by-products.

As for the structure of reaction products, the ether linkages are not very strong and may undergo degradation or hydrolysis under mild conditions. When the reaction is further induced by a higher temper-

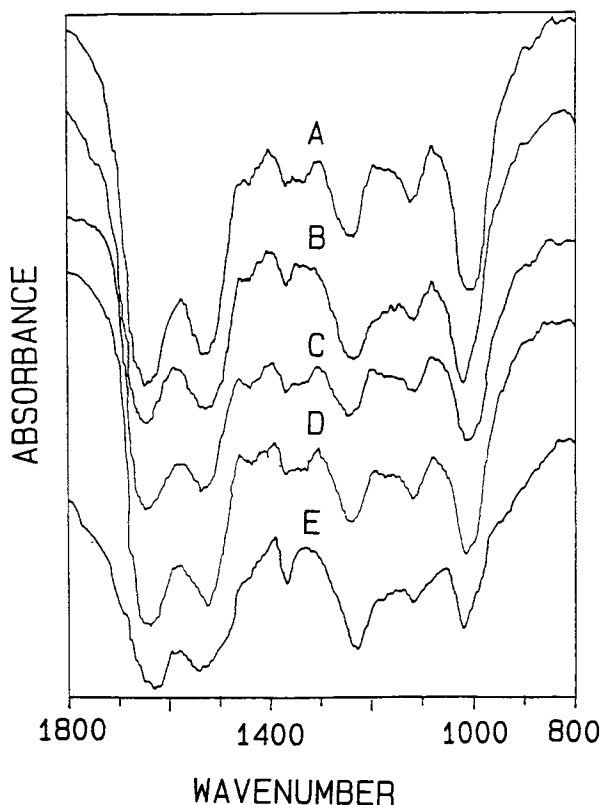


**Figure 1** IR spectra: (A) UF resin before curing, (B) UF resin after curing, (C) LS-OB.

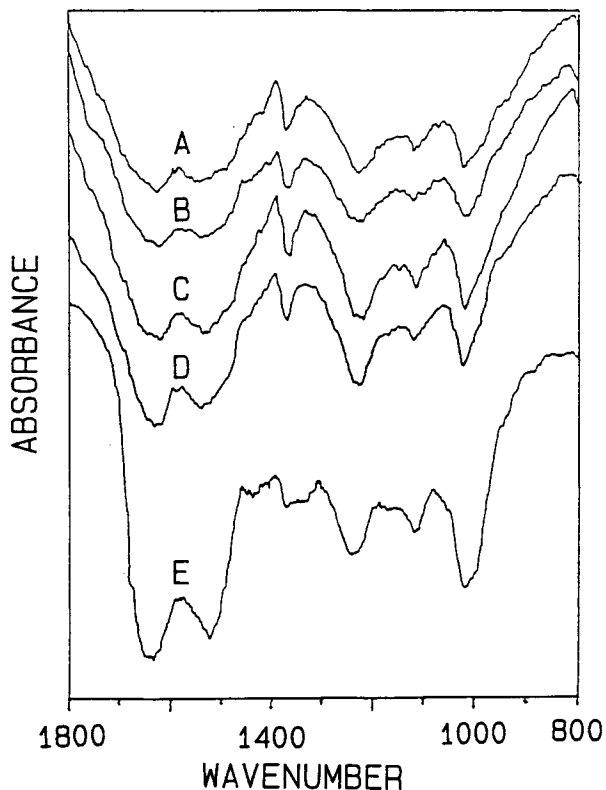
ature or by catalyzing to a lower pH, a *methylene bridge* linkage can be formed. This linkage is more stable and displays a better resistance to degradation and hydrolysis.

### IR Spectra of UF Resin and Its Mixtures with LS-OB

The condensation mechanism between LS-OB and UF resin can be revealed from the difference between the IR spectra of the resin and those of its mixtures before and after curing. However, condensation of UF resin is a pH-sensitive reaction that can be accelerated by heat.<sup>6,8</sup> For preparing a representative uncured sample for IR measurement, precaution should be taken to prevent UF resin from undergoing condensation, if the sample had to be exposed to heat for drying. Toward this end, the pH of liquid resin and its mixtures was adjusted to 9.0 or above with alkaline solutions, since the resin could not be cured at such pH. Another resin sample was treated in a way where no pH adjustment of solutions was



**Figure 2** IR spectra of mixtures of LS-OB and UF resin before curing: (A) 20% LS-ONa, (B) 40% LS-ONa, (C) 20% LS-OH<sub>4</sub>, (D) 30% LS-OH<sub>4</sub>, and (E) 30% LS-OH<sub>4</sub> after curing.



**Figure 3** IR spectra of mixture of LS-OB and UF resin after curing: (A) 20% LS-ONa, (B) 40% LS-ONa, (C) 20% LS-OH<sub>4</sub>, (D) 30% LS-OH<sub>4</sub>, and (E) 30% LS-OH<sub>4</sub> before curing.

made but the catalyst was presented so that the resin could be cured during heating at high temperature. The IR results thus obtained are presented in Figures 1-3, from which the curing mechanism of UF-(LS-OB) mixtures could be revealed.

### UF Resin

Figure 1 presents the characteristic IR spectra of UF resin before (curve A) and after (curve B) curing. It can be found that, before curing, UF resin contains hydroxymethyl or methylol groups ( $1010\text{ cm}^{-1}$ ) and dimethylene ether ( $830\text{ cm}^{-1}$ ). Methylol is the product of addition reaction between urea and formaldehyde, and dimethylene ether is the condensation product of two DMU structures. After curing, these two structures decrease, and methylene increases ( $1380\text{ cm}^{-1}$ ). These results agree with the observation of other researchers.<sup>9,10</sup>

### LS-OB

Figure 1 presents also the IR characteristics of lignosulfonate (curve C). The very intense band at

1030  $\text{cm}^{-1}$  and, those between 1100 and 1250  $\text{cm}^{-1}$  might be ascribable mainly to the sulfonic acid structure. A pronounced vibration of the aromatic rings appears at 1500  $\text{cm}^{-1}$ , and the band at 1600  $\text{cm}^{-1}$  is primarily due to the symmetric stretching of carboxyl groups and the ring vibration. The bands at 1700 and 1750  $\text{cm}^{-1}$  may be attributed to the carbonyl groups.

### Condensation between LS-OB and UF Resin

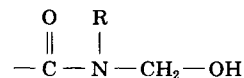
Figures 2 and 3 resume the absorption of UF-(LS-OB) mixtures, in different proportions of two lignosulfonate salts (LS- $\text{ONH}_4$  and LS- $\text{ONa}$ ). The former figure shows mainly the spectra of mixtures before curing, except that curve *E* is for one mixture after curing and is presented for the purpose of comparison, while the latter shows those after curing. One can see that the spectra of the two salts ( $\text{NH}_4$  and  $\text{Na}$ ) differ very little from each other.

The dimethylene ether and alkyl ether bridges are indicated, respectively, by the bands at 830 and 1120  $\text{cm}^{-1}$ . The band of methylol group (1010  $\text{cm}^{-1}$ ) and that of sulfonic acid group (1030  $\text{cm}^{-1}$ ) may overlap at 1020  $\text{cm}^{-1}$ , while the bands for aromatic alkyl ether bridge and for C—N stretching vibration may overlap at 1240  $\text{cm}^{-1}$ . N—H stretching vibration is characterized at 1330  $\text{cm}^{-1}$ , and methylene bridge is identified at 1370  $\text{cm}^{-1}$ .

It is interesting to notice, after mixed with UF resin, the disappearance of the characteristic bands of carbonyl groups in LS-OB at 1700 and 1750  $\text{cm}^{-1}$  and the broadening aromatic bands at 1500 and 1600  $\text{cm}^{-1}$ ; while sulfonic acid groups (1030  $\text{cm}^{-1}$ ) still remained, indicating the inactive characteristics of sulfonic groups under this circumstance. From this observation, one might consider that the main functional groups of lignin probably react readily with UF resin even at room temperature (i.e., before curing; see Fig. 2), or that the bands of LS-OB are overlapped by those of UF resin. On the other hand, one can find that almost all the characteristic bands of UF resin still exist after mixed with LS-OB. It leads to a hypothesis that UF resin might react with LS-OB in the same way as it reacts with itself. The methylene and dimethylene ether bridges could thus be produced and certain dimethylene ether bridges could change into methylene bridges with the release of formaldehyde and water.

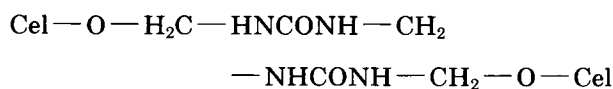
### Mechanism of Condensation

Without the presence of LS-OB, the active site in UF resin is the hydroxymethyl group of methylol-urea:



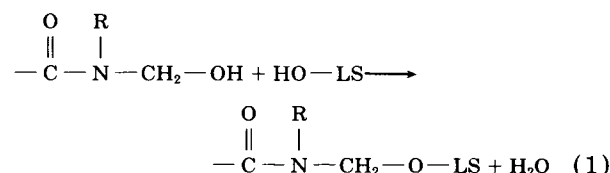
which reacts with other hydroxymethyl groups to form either ether bonds or ethylene bridges and results in a high crosslinking matrix. In the presence of LS-OB, the functional groups contained in the oxidized lignosulfonate and carbohydrate (i.e., hydroxyl, carbonyl, and phenolic groups) might display high relative reactivities toward the functional groups in the UF resin. The ether and ethylene bridges would thus form between LS-OB and UF molecules during condensation.

It has been reported that UF resin could be modified with alcohols containing a higher number of carbon atoms (e.g., *n*-butanol) to impart stability and flexibility.<sup>6,8</sup> It has also been reported that UF resin could readily condense with cellulose through ether linkages.<sup>7</sup>

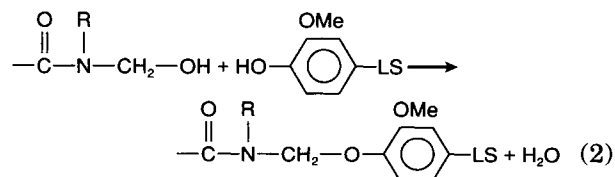


According to those descriptions, methylol-urea could condense easily with the materials that contain hydroxyl groups. Similarly, one may suppose that UF resin could undergo condensation and form the ether or methylene linkages with the different functional groups on LS-OB molecules through the following reactions:

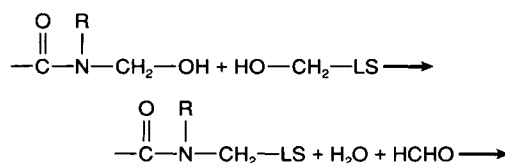
Ether linkage formed with aliphatic OH group

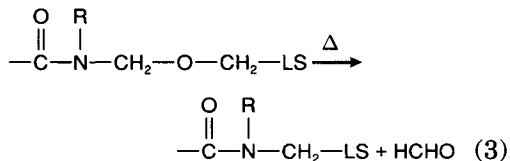


Ether linkage formed with phenolic OH group

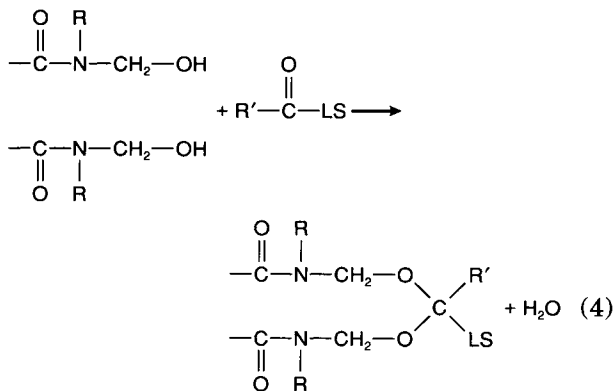


Methylene linkage formed with hydroxymethyl



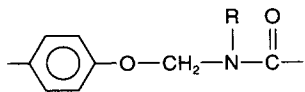


Ether linkage formed with carbonyl



where R is H or other alkyl groups and LS is lignosulfonate or carbohydrate.

This hypothesis may be supported by examining the IR spectra. The conversion of the methylol group during condensation in all of the four reactions may explain the decline of the methylol band at  $1020 \text{ cm}^{-1}$ . There might be an intermediate formation of dimethylene ether ( $830 \text{ cm}^{-1}$ ) and alkyl ether bonds ( $1120 \text{ cm}^{-1}$ ) through reactions [1] and [4], but these bonds would diminish afterward due to reaction [3]. During reaction [3] the methylene bridge was formed that increased the band at  $1370 \text{ cm}^{-1}$ . Reaction [2] may explain the increase at  $1240 \text{ cm}^{-1}$  that overlaps the C—N stretching vibration and aromatic alkyl ether bands, indicating the formation of aromatic alkyl ether bridges during condensation:



The occurrence of reaction [4] could be accelerated in the presence of oxidized lignosulfonate, since the concentration of carbonyl groups in lignosulfonate was increased to about 1.5 times by oxidation, as found in previous studies<sup>4</sup> and shown in Table I. In other words, the oxidized lignosulfonate, possessing a higher carbonyl content, had a higher reactivity toward UF than the unoxidized one.

## Oxidized Lignosulfonate in Particleboards

### Effect of Oxidation Time

Figure 4 presents the results obtained with a 30% substitution of LS-ONa for UF in adhesive formu-

**Table I** Oxidation of Lignosulfonate at  $150^\circ\text{C}$  (Ref. 4)

Oxidation Time (min)	Carbonyl Content (mmol/g)
0	0.72
5	0.82
15	0.89
30	0.96
60	1.07
120	1.12
180	1.16

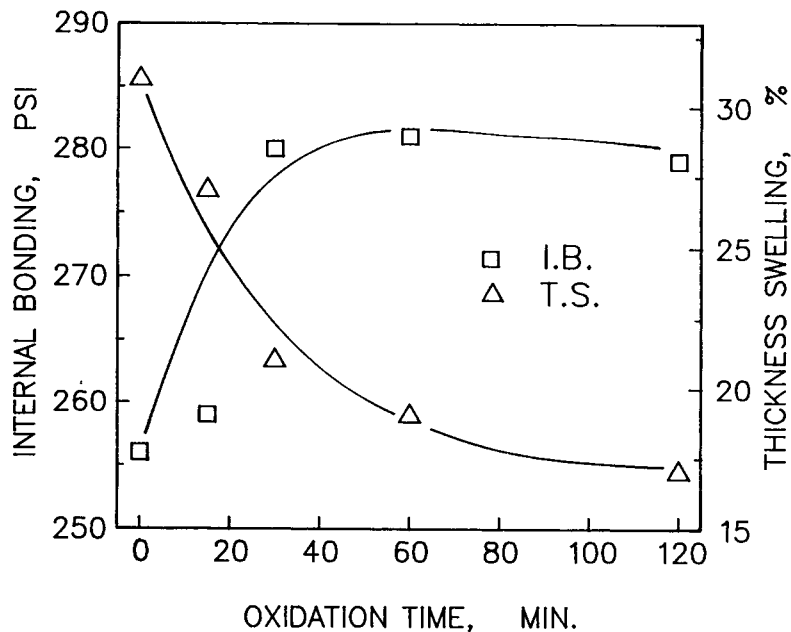
Carbonyl group of the crude lignosulfonate was  $0.49 \text{ mmol/g}$ ; it was increased to  $0.72 \text{ mmol/g}$  during the heating-up period.

lation. The internal bond (IB) of particleboard was increased with the increasing of oxidation time of lignosulfonate from 256 to 280 psi during the first 30 min of reaction, and practically unaffected with further oxidation. The thickness swelling (TS) was also improved considerably by oxidation; it dropped from 31 to 21% during the first 30 min, then dropped slightly with longer oxidation time.

### Effect of LS-OB Content

As mentioned previously,<sup>4,5</sup> oxidation of LS-OB alters its functional groups, as well as the molecular weight distribution of lignosulfonate; the content of carbonyl group could be substantially increased. This kind of modification improved the reactivity of LS-OB toward UF resin, so that LS-OB would readily condense with dimethylol urea through ether bond or methylene bridge. When applied to particleboard manufacturing, the high surface activity of LS-OB would reduce the surface tension of binder solution, and thus facilitate the distribution of the solution on wood particles. It was expected, therefore, that LS-OB could be used to replace a part of UF resin as the binder.

Figures 5 and 6 show the results obtained with the adhesives of different proportions between LS-OB and UF resin. Prior to preparing the adhesive mixture, the pH of LS-OB solutions (60 min of oxidation) was adjusted to 4.5 or 5.0 with NaOH. From these figures, it is evident that LS-OB had a positive effect on particleboard properties. An augmentation in IB could be obtained when the LS-OB content in adhesive was in the range of 10–40%; beyond this range, a sharp detriment appeared. No effect on TS was observed when the LS-OB content was less than 40%; the TS value was kept practically constant



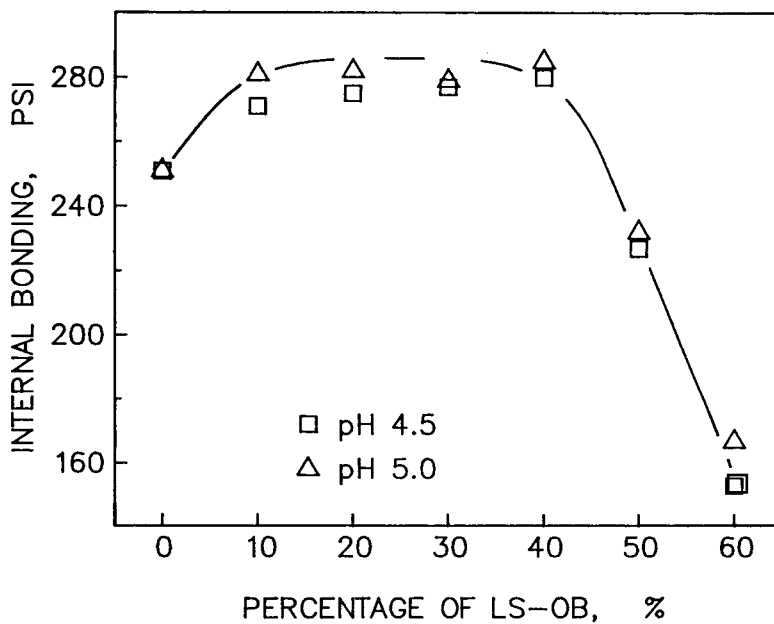
**Figure 4** Variation of IB and TS of particleboard as a function of oxidation time of lignosulfonate.

around 20%. The value jumped to 35% if the ratio of LS-OB to UF resin was 1 : 1.

The pH of LS-OB solution had no significant effect on particleboard properties, although the solution with a higher pH (i.e., 5) appeared to yield a marginally superior IB and TS in Figures 5 and 6.

**CONCLUSIONS**

The oxidized lignosulphonate, LS-OB, could display a high relative reactivity toward UF resin through the condensation between carbonyl groups in LS-OB and methylol groups in UF resin. Ether and



**Figure 5** Effect of LS-OB content on the internal bond of particleboard.

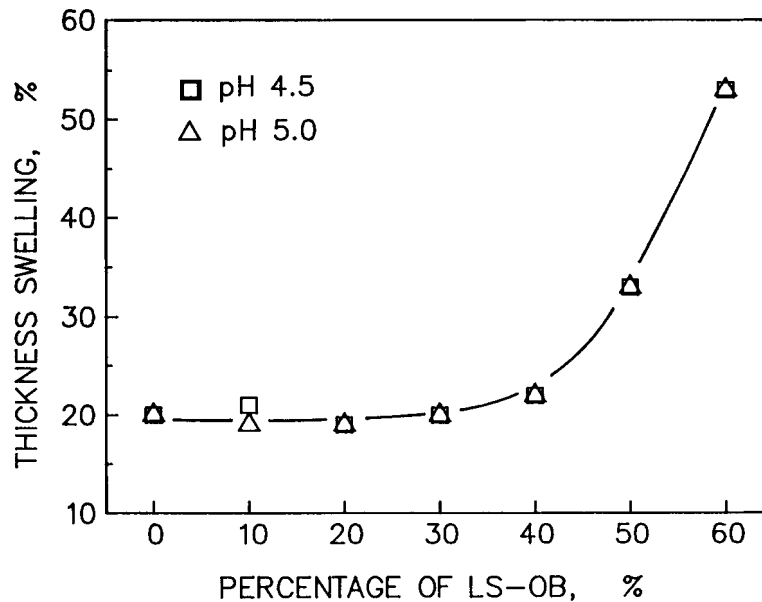


Figure 6 Effect of LS-OB content on the thickness swelling of particleboard.

methylene bridges could be formed, even at low temperature (e.g., room temperature). At higher temperature (e.g., 150–180°C), more ether bonds would be formed but some of them might transform into methylene bridges; the later would be better water resistant.

LS-OB could be utilized in the adhesive formulation for particleboards. A substitution of LS-OB for UF resin in the range of 10–40% had positive effect on certain properties of particleboard, such as internal bond. Beyond this range, detrimental effects could arise, suggesting that the quantity of active groups in LS-OB was not sufficient to polycondense with UF resin so as to transform 100% into tridimensional matrix. Future work in our laboratory will be conducted to develop the adequate oxidation processes that would further promote the reactivity of lignosulfonate.

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