Self-Condensation of Oxidized Lignosulfonate. II. Condensation Behaviors

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SYNOPSIS

Studies have been made on the principal parameters that affect the self-condensation of oxidized lignosulfonate, such as lignin content, pH, temperature, time of hot pressing, and oxidation. During condensation, the hydroxyl groups in both the lignosulfonate and carbohydrate molecules could react with carboxyl, sulphonic acid, and carbonyl groups to form an ester bond and result in (hemi)ketal and (hemi)acetal structures. These structures made condensation products having excellent resistance in water and in alkaline solutions. The results also demonstrated that the oxidized lignosulfonate could be condensed at a higher rate than could the untreated one.

INTRODUCTION

For the past several decades, to improve the utilization of lignin in wood-based panel industries, many attempts have been made to elucidate the reaction mechanism of lignin with formaldehyde and to improve the reactivity of hydroxymethyl lignin. It has been well known that, during the reaction of hydroxymethyl lignin with phenol-formaldehyde (PF) resin, condensation could take place between hydroxymethyl lignin molecules or between PF resin and hydroxymethyl lignin molecules through methylene bridges.[1] Lignin could react with formaldehyde to form different hydroxymethyl phenylpropane units that would subsequently condense with other phenylpropane units in lignin molecules or with phenol in PF resin and produce a high crosslinkage resin. From the viewpoint of the "methylene bridge," the hydroxymethylating rate of lignin and reactivity of hydroxymethyl groups are the important parameters that affect the outcomes of condensation. However, very few works have yet been successful in obtaining lignin derivatives possessing a high reactivity. One of the main reasons was the fact that the ortho- and para-positions of the lignin aromatic rings are occupied to a great extent by methoxyl groups and propane side chains, which hinder the reaction of lignin with formaldehyde and hinder the further condensation with other lignin molecules as well.[2]

In our recent report,[3] the condensation phenomenon of the lignosulfonate (LS) derivative has been presented. This derivative manifested a high performance during thermal condensation, and the condensed product displayed an excellent resistance to water, enabling it to be used in resin formulation alone or to replace a part of UF resin while the operation conditions could be accepted by industries.

The objective of the present work was to study the effect of operating parameters on polycondensation, such as oxidation time of LS, lignin content, and pH of samples, as well as to investigate the alkaline resistance of the condensation product. In light of the results, the polycondensation mechanism of oxidized LS would be suggested. The physical properties of the cured specimens have been studied on our research and will be published elsewhere.

EXPERIMENTAL

Materials

The lignin (LS-BD) used was a commercial product of calcium lignosulfonate (Daishowa Chemicals,

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Quebec, Canada). Pure lignosulfonate (LS-D) was prepared by dialysis with water (membrane: Model B, Pope Scientific Inc; molecular weight cutoff: 8000–10,000). The high and low molecular weight fractions (HMW and LMW) were obtained by ultrafiltration of LS-BD using a polysulfone membrane filter having a nominal molecular weight limit of 10,000 (Immersible CX-10, Millipore Corp.). Carboxymethyl cellulose (CMC, Sigma Chemical Company, St. Louis, MO) and polyvinyl alcohol resin (PV, 99–100% hydrolyzed, St Lawrence Chemical) were in chemical-pure grade and used as received.

Oxidation

Aqueous solution of lignosulfonate (5% by weight) was heated in a stainless-steel autoclave (Mode M/K 409, M/K Systems Inc.) equipped with a circulation pump. After reaching the required temperature, oxygen was introduced to raise its partial pressure to 2.5 atm. Samples were withdrawn for analysis at 0, 5, 10, 30, 60, and 120 min after reaction.

The pH of all solutions was adjusted to a desired value with sulfuric acid; before and after pH adjusting, the precipitate of calcium base was removed by filtration. The solutions were dried by lyophilization (Freeze Dry-12, LABCONCO Corp., Kansas, MO), followed by grounding the solid into powders, which were then hot-pressed under given temperatures and times.

One series of impurity-lignin mixtures were prepared by mixing a 2A120 sample (LS oxidized for 120 min and acidified to pH 1.20) with 1, 2.5, and 5% CMC; another series was prepared with PV.

Hot Pressing

About 1 g of sample powder was confined in a model hole (1.6 mm in thickness) that was sandwiched by two aluminum plates. Hot press was carried out with a laboratory oil-hydraulic press (Duke Corporation) under a pressure of 2.9 MPa and at a predetermined temperature.

Characterizations

Insolubility

To indicate the curing ability of LS and its acidified oxidation derivative (AOL), the insolubility of the hot-pressed product in water, as well as in alkaline solution, was measured. The measurement was conducted by soaking about 3 g of samples in 100 mL

boiling distilled water or 0.5 N NaOH solution for 1 h. The solid residue was filtered, washed with distilled water, and oven-dried. Then,

$$\text{Insolubility}, \% = (W_f/W_i) \times 100$$

where W_f is the weight of the final solid residue, and W_i, the initial sample weight.

Total and Phenolic Hydroxyl Contents

The phenolic hydroxyl content of samples was determined by UV chromatograph that involved the measurement of the difference in absorption between an alkaline and acidic solutions at 250 nm.[4] The total OH content was determined through acytylation of OH groups in LS molecules[5,6] and was expressed in terms of equivalent acetic acid. Then, the difference between total-OH and phenolic-OH contents indicated the amount of aliphatic OH.

Carbonyl Group

Carbonyl content was determined according to the method that measured the amount of HCl liberated during a reaction between hydroxylamine hydrochloride and carbonyl groups[7] and was expressed in terms of equivalent HCl.

All data reported in this work represent the average value obtained from triplicate determinations.

RESULTS AND DISCUSSION

Effect of LS Content

The testing samples whose LS content ranged from 34.7% (LMW) to 100% (LS-D) were hot-pressed at 150°C, and the results are summarized in Table I, whereas the results obtained with 4 min of hot-pressing are illustrated in Figure 1. One can find that, both in water and in alkaline solutions, insolubility was increased with the increment of LS content (more precisely, lignosulfonic acid), indicating the dependence of crosslinkage on LS content during thermal polycondensation between lignosulfonates and carbohydrates. When LS content was inferior to 60%, the insolubilities in water was increased slightly with the increase of LS content; an increase of about 5% in insolubility was obtained when LS content varied from 34.7 to 60%. Beyond this point, insolubility rose sharply, from 73.1% to over 90%, if the LS content was increased from 61 to 79%. The same phenomena could be observed if the thermal-condensed sample was treated with alkaline solution.

Table I   Effect of LS Content on Condensation

Sample	Lignosulfonate Content (%)	Pressing Time (min)	Insolubility in Water (%)	Insolubility in Alkaline Solution (%)
LS-D	100	2	91.6	92.2
		4	92.9	94.3
HMW	79.1	2	90.3	80.0
		4	90.6	83.3
		6	91.9	85.9
LS-BD	61.0	2	62.8	53.0
		4	73.1	67.5
		6	74.7	70.3
LMW	34.7	2	66.0	63.5
		4	67.3	65.6
		6	69.6	67.7

Pressing temperature: 150°C; pH of sample before drying: 1.15.

These results revealed that LS content had a positive effect on the polycondensation rate: The higher the LS content of sample was, the higher the insolubility would be. In the case of pure lignosulfonate, LS-D, polycondensation could readily occur even at low temperature. This was indicated by the observation that after drying by lyophilization, part of LS-D could not be dissolved either in water or in alkaline solution. As a fact, a lower LS content signified a higher sugar content in a sample; one could thus conclude that a higher sugar content of sample would diminish polycondensation. It should be pointed out that this conclusion was a contradiction with those drawn from some previous research.[8,9] Those authors mentioned that the LMW fraction of LS ($M_w < 10,000$) was obtained by ultrafiltration and contained 50% reducing sugar and was com-

patible with PF in preparation of thermosetting resin and that this resin performed well, while the HMW ($M_w > 10,000$) portion failed to function as a thermosetting binder.

Effect of Oxidation Time

It can be noticed from Table II and Figure 2 that prolonging oxidation time could promote the polycondensation of AOL (expressed as insolubility), especially in the first 5 min. As was found in our previous work, functional groups in LS molecules had changed greatly during oxidation.[3] After 120 min of oxidation, the carbonyl group was increased about 2.4 times (from 0.49 to 1.16 mmol/g) and the carboxyl group also increased, for the pH dropped from 4.06 to 2.08. Meanwhile, phenolic OH and aliphatic OH groups decreased to 0.83 and 1.51 mmol/g, respectively. One would expect that, after oxidation, all changes in the functional groups could increase the condensation activity of AOL.

Effect of pH

The pH of the sample solution before drying had an enormous effect on the subsequent thermal polycondensation. The results, as summarized in Table III and illustrated in Figure 3, show evidently that a pH higher than 1.2 brought forth an adverse effect on polycondensation (expressed in terms of insolubility). It was speculated that, at low pH, the excessive mineral acid (i.e., sulfuric acid used in the present work) would cause readily dehydration be-
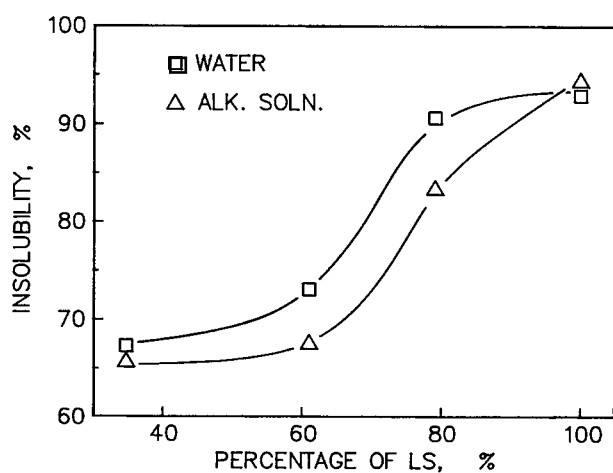

Figure 1   Effect of lignosulfonate content.

Table II Effect of Oxidation Time on Hot Pressing

| | Oxidation | | | | |
Sample	Temp (°C)	Time (min)	pH	Insolubility in Water (%)	Insolubility in Alkaline Solution (%)
LS-BD	150	0	1.15	73.1	67.5
2A005	150	5	1.15	78.6	71.3
2A015	150	15	1.15	79.5	72.3
2A030	150	30	1.15	79.9	73.0
2A060	150	60	1.15	80.4	73.8
2A120	150	120	1.15	81.0	74.7

Pressing at 150°C for 4 min.

tween certain functional groups in LS or AOL molecules during hot-pressing, thus promoting the intermolecular crosslinkage. Consequently, with a lower pH, the hot-pressed lignosulfonate could display a higher insolubility in water or alkaline solution. When pH varied from 1.15 to 1.40, the insolubility in water dropped moderately from 81.0 to 78.6% for the oxidized sample (2A120), but considerably from 73.1 to 48.3% for the unoxidized one (LS-BD). As to the insolubility in alkaline solution, with the same variation of pH from 1.15 to 1.40, a drop from 74.7 to 65.1% was observed for oxidized sample 2A120 and a drastic one from 67.5 to 19.6% for unoxidized sample LS-BD. It was obvious that the oxidized lignosulfonate was more active, as compared to the unoxidized one, in thermal condensation and its condensed product possessed much better water or alkaline resistance.

However, if the solution pH was adjusted to 1.7, no satisfactory crosslinkage could be obtained ther-

mally, even with the oxidized LS. The hot-pressed sample in this case displayed a water insolubility only around 56%, and it was almost completely soluble in alkaline solution (insolubility = 0.4%). These results revealed that, under different pH, there existed two sorts of polycondensed lignosulfonates: One had excellent resistance both in water and in alkaline solution; another might be well resistant to water but soluble in alkaline solution.

Condensation Mechanism

According to the results mentioned above, it could be suspected that, in the presence of a mineral acid, H_2SO_4, certain reactions, involving dehydration, would occur between the functional groups in LS and AOL by dehydration:

1. In presence of acid catalyst, some ester structures could be formed between hydroxyl groups (i.e., phenolic and aliphatic OH) and acid groups (e.g., sulphonic group and carboxyl group). The possible scheme would be as follows:
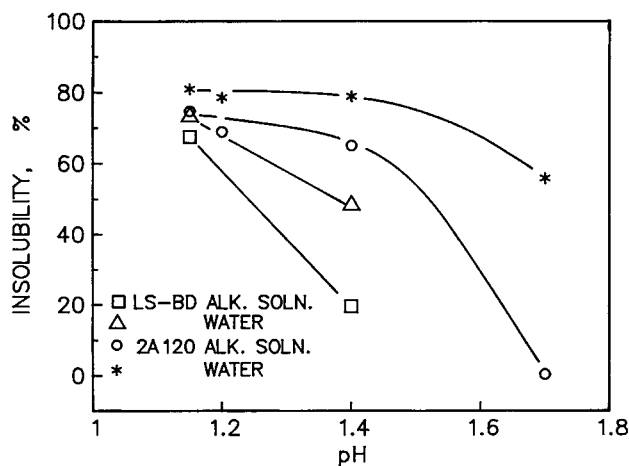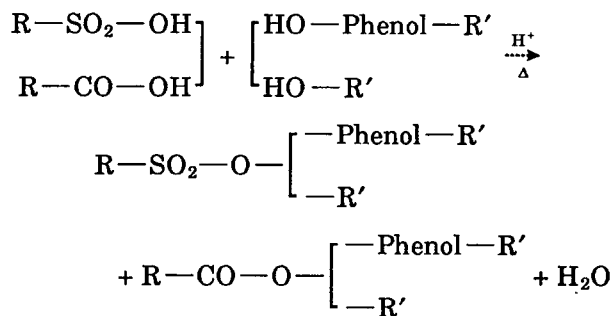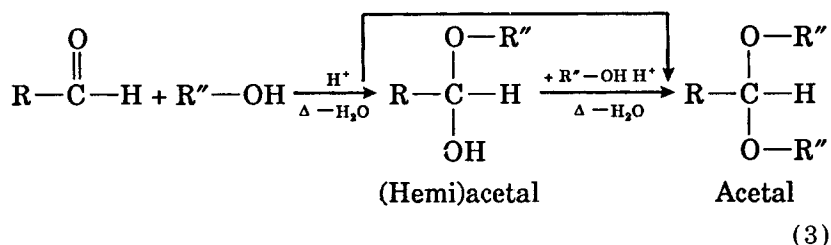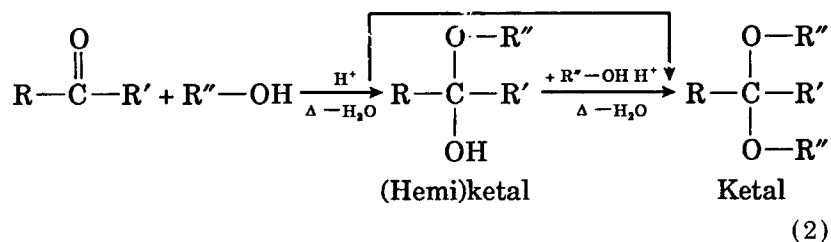
Figure 2 Effect of sample's pH.

$$\begin{bmatrix} R—SO_2—OH \\ R—CO—OH \end{bmatrix} + \begin{bmatrix} HO—Phenol—R' \\ HO—R' \end{bmatrix} \xrightarrow[\Delta]{H^+}$$

$$R—SO_2—O—\begin{bmatrix} —Phenol—R' \\ —R' \end{bmatrix}$$

$$+ R—CO—O—\begin{bmatrix} —Phenol—R' \\ —R' \end{bmatrix} + H_2O$$

(1)

2. Under a stronger acid condition, a carbonyl group, such as aldehyde and ketone struc-

tures, would react with OH groups (alcohol structure) to form (hemi)ketal and (hemi)-acetal, as shown in Eqs. (2) and (3):

$$R—\overset{\overset{O}{\parallel}}{C}—R' + R''—OH \xrightarrow[\Delta\ -H_2O]{H^+} R—\overset{\overset{O\cdot-R''}{|}}{\underset{\underset{OH}{|}}{C}}—R' \xrightarrow[\Delta\ -H_2O]{+R'-OH\ H^+} R—\overset{\overset{O-R''}{|}}{\underset{\underset{O-R''}{|}}{C}}—R'$$

(Hemi)ketal   Ketal

(2)

$$R—\overset{\overset{O}{\parallel}}{C}—H + R''—OH \xrightarrow[\Delta\ -H_2O]{H^+} R—\overset{\overset{O-R''}{|}}{\underset{\underset{OH}{|}}{C}}—H \xrightarrow[\Delta\ -H_2O]{+R'-OH\ H^+} R—\overset{\overset{O-R''}{|}}{\underset{\underset{O-R''}{|}}{C}}—H$$

(Hemi)acetal   Acetal

(3)

These two kinds of reactions could occur under milder conditions (i.e., temperature and pH) than that for condensation of hydroxymethyl lignin. Thus, under the conditions employed in the present work, the rather high temperature and acidity would surely accelerate the reactions and favor the formation of ester, (hemi)ketal and/or ketal, and (hemi)acetal and/or acetal structures. These structures enabled the reaction products to display good alkaline resistance. As a result, the hot-pressed LS and AOL could exhibit good insolubility both in water and in alkaline solutions.

To verify this hypothesis, CMC and PV were added to lignosulfonate during hot-pressing, since these two compounds are of long chains and consist of a great quantity of OH groups. The results are presented in Table IV and also in Figures 4 and 5, which show, respectively, the effect of additives on insolubility in water and in alkaline solution. It can

be seen that a small amount of CMC would increase condensation of LS. The maximum insolubility in water occurred with 1% CMC (Fig. 4): It attained 81.4 and 84.5% at 150 and 160°C, respectively, being 2.8 and 2.4% higher than those without CMC at the same hot-pressing temperature and time. However, if the CMC charge was higher than 1%, insolubility was decreased with the increase of CMC. As to the addition of PV, the insolubility in water of LS was increased steadily with the increment of PV, from 78.6 and 82.1% without PV to 82.2 and 86.5% with 5% PV, at pressing temperatures of 150 and 160°C, respectively.

A comparison of Figures 4 and 5 indicates that a similar trend occurred in the insolubility in alkaline

Table III   Effect of pH on Hot Pressing

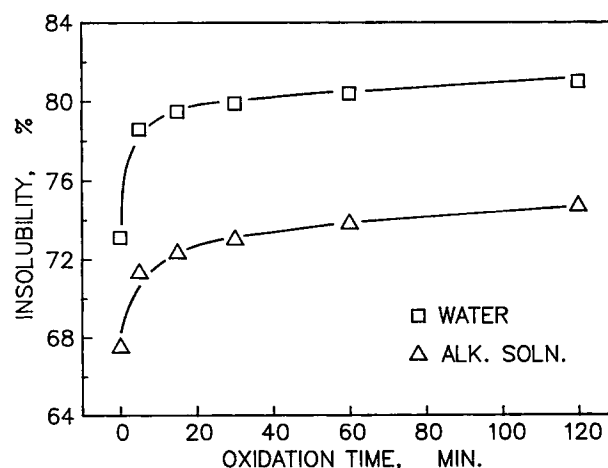| Sample	pH	Insolubility in Water (%)	Insolubility in Alkaline Solution (%)
LS-BD	1.15	73.1	67.5
	1.40	48.3	19.6
2A120	1.15	81.0	74.7
	1.20	78.6	72.1
	1.40	78.9	65.1
	1.70	55.8	0.4

Figure 3   Effect of oxidation time of lignosulfonate with oxygen.

Table IV Results of Hot-Pressing with the Addition of CMC and PV

Sample	Addition Content	pH	Temp (°C)	Time (min)	Insolubility in Water (%)	Insolubility in Alkaline Solution (%)
LS-BD	0	1.20	150	2	62.8	53.0
				4	73.1	67.5
				6	74.7	70.3
			160	1	69.2	55.3
				2	70.8	62.4
				4	79.1	73.1
2A120	0	1.20	150	2	72.4	57.3
				4	78.6	68.8
				6	81.1	72.9
			160	1	70.7	58.2
				2	79.3	69.6
				4	82.1	75.0
	1% CMC	1.20	150	2	77.6	65.3
				4	81.4	74.2
				6	84.6	78.8
			160	2	79.7	71.0
				4	84.5	77.8
	2.5% CMC	1.20	150	2	73.1	56.4
				4	78.9	69.1
				6	81.3	73.1
			160	2	79.0	69.2
				4	82.1	75.0
	5% CMC	1.20	150	2	72.4	54.4
				4	78.6	68.0
				6	81.3	71.8
			160	2	78.2	68.0
				4	80.3	72.4
	1% PV	1.20	150	2	74.4	59.0
				4	78.9	69.9
				6	81.6	75.2
			160	2	79.6	69.5
				4	83.1	76.0
	2.5% PV	1.20	150	2	75.1	63.1
				4	79.7	71.0
				6	82.2	76.0
			160	2	81.4	72.3
				4	85.6	78.6
	5% PV	1.20	150	2	76.3	65.1
				4	82.2	74.1
				6	84.3	78.1
			160	2	83.3	75.6
				4	86.5	79.6

solution. One could thus suggest that CMC and PV would act as an intermediate: Their OH groups could condense with carboxyl, sulphonic, and carbonyl groups, existing in a great quantity in LS molecules, to form ester bonds according to the eq. (1) and to form ketal and acetal bonds according to the eqs. (2) and (3). Because of their long straight chains, they could simultaneously condense with numerous LS molecules, enhancing quickly the crosslinkage degree of LS and, consequently, increasing the insolubility both in water and in alkaline solutions.

However, no such effect was observed with addition of sugar, whose molecular weight was rather low. One sugar molecule could react with LS, but might fail to condense simultaneously with several LS molecules. On the other hand, several sugar molecules condensed with LS might occupy the reactive cites of LS molecule and thus hinder the further condensation.

CONCLUSION

Lignosulfonate and its oxidized derivatives could polycondense with each other, or with some materials containing OH groups, by ester or by ketal and acetal bonds. Oxidation of LS and acidity of reaction medium were the essential parameters determining the condensation rate. Oxidation could increase the acid (carboxyl) and carbonyl groups, meanwhile maintaining a certain amount of OH groups, which would be the active centers during condensation. Mineral acid could act as a catalyst that accelerated polycondensation by dehydration. It is worthwhile to point out that the acidified oxidized lignosulfonate (AOL) was of higher reactivity and sensitivity at moderate temperature and pressure than was other modified lignin. The hot-pressed AOL displayed
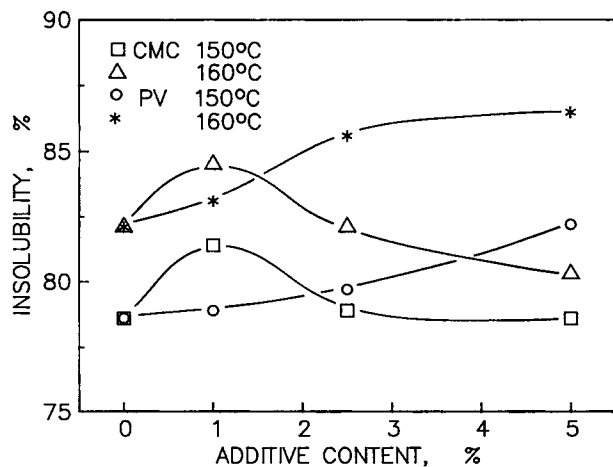
Figure 4   Effect of CMC and PV contents on insolubility in water.
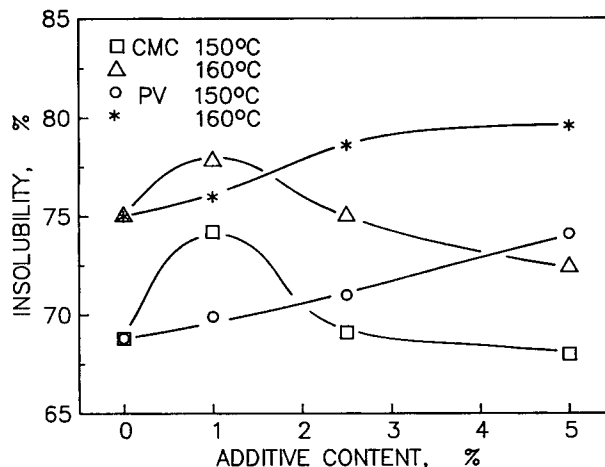
Figure 5   Effect of CMC and PV contents on insolubility in alkaline solution.

certain positive characteristics of a thermal-setting resin, promising its application to the field of adhesives, such as binders in wood panel production. Studies on such application have been undertaken in our institute and a part of results will be soon published elsewhere.

REFERENCES

1. S. Jolly, S. P. Singh, S. V. Singh, and R. C. Gupta, *Cellulose Chem. Technol.,* **16,** 511 (1982).
2. K. G. Forss and A. Fuhrmann, *Forest Products J.,* **29**(7), 39 (1979).
3. R. Chen and G. Wu, in *Fifth International Symposium on Wood and Pulping Chemistry,* Raleigh, North Carolina, 1989, p. 39.
4. Daishowa Chemicals (Québec, Canada), *Standard Test Method: TM-15,* 1986.
5. U. Freudenberg and H. Schluter, *Chem. Ber.,* **88,** 617–618 (1955).
6. B. Person, *Svensk Papperstidn,* **60,** 158 (1957).
7. E. Adler and J. Gierer, *Die Chemie der Pflanzeyzellwand,* Springer-Verlag, Berlin, 1957, p. 446.
8. K. C. Shen and D. P. C. Fung, Forintek Canada Corp. Technical Report, 509-E, 1979.
9. K. C. Shen and L. Calve, *Adhesives Age.,* **23**(8), 25 (1980).