Wood Adhesives Based on Lignin Wastes: Influence of the Carbohydrates in the Polymerization of Spent Sulfite Liquor*

L. CALVÉ and J. M. J. FRÉCHET, *Department of Wood Composites, Forintek Canada Corp., 800 Montreal Rd., Ottawa, K1G 3Z5, Ontario, Canada*, and *Department of Chemistry, University of Ottawa, Ottawa, K1N 9B4, Ontario, Canada*

Synopsis

The influence of carbohydrates on the thermosetting properties of ammonium-spent sulfite liquor (NH_4SSL) was studied using various fractions of the liquor obtained by ultrafiltration. While a low molecular weight carbohydrate-rich fraction thermoset readily, a higher molecular weight sugar-free fraction failed to thermoset. Optimum results in the use of NH_4SSL as a binder for wood particles were obtained by adjusting the carbohydrate to lignin ratio through addition of carbohydrates to the liquor. Similarly, several sugars used alone as binders without addition of lignin gave satisfactory results at slightly higher press temperatures. A study of various sugars and similar molecules in the binding of wood particles suggested that a combination of ene-aldehyde or keto-alcohol functionalities was likely to produce good results. Condensations involving sugars were affected by such variables as carbohydrate chain length, moisture content, acid catalysis, and press temperature.

INTRODUCTION

In Canada alone, the pulp and paper industry produces daily over 4000 metric tons of dry solids spent sulfite liquor (SSL), a portion of which is used as a low grade fuel, while most of the rest has to be discarded. In general, SSL contains over 60% of lignin derivatives and also significant amounts of sugars resulting mainly from the partial hydrolysis of hemicelluloses. As lignin materials are generally thought of as the natural bonding agents of wood,[1] considerable efforts have been devoted to the development of new bonding agents for wood particles based on the lignin waste materials. A few years ago, it was found that calcium spent sulfite liquor (CaSSL) could be used as a binder for wood composites after treatment with sulfuric acid.[2] More recent work from our laboratory[3] showed that ammonium spent sulfite liquor (NH_4SSL) could also be used as a thermosetting binder for wood products, but, unlike CaSSL, no prior acidification was required for the thermal polymerization to occur. It appeared likely that, for both of these processes, lignosulfonic acid is released either through reaction with sulfuric acid (CaSSL) or through thermal decomposition (NH_4SSL). The thermal polymerization of free lignosulfonic acid would then be responsible, at least in part, for the binding properties of the treated spent sulfite liquors.

Although the exact structure of lignin is still unknown due to its extreme complexity and variations arising from the nature of the wood and the processing

---

* Taken in part from L. Calvé's thesis, University of Ottawa, 1980.

Journal of Applied Polymer Science, Vol. 28, 1969–1980 (1983)

CCC 0021-8995/83/061969-12$02.20

TABLE I
Effect of Fractionation and Additives on Bonding Properties of NH_4SSL

Crude NH_4SSL (wt %)	Ultrafiltrated MW 0–5000 (wt %)	Ultrafiltrated MW 5000 and up (wt %)	Additive (wt %)	Lignin (wt %)	Reducing sugars (wt %)	N (%)	S (%)	TS (Nm)[c]
100	0	0	0	68	22	2.8	6.5	2.0
50	0	0	50[a]	34	61	1.4	3.3	7.1
73	0	0	27[b]	50	—	2.0	4.7	6.6
0	100	0	0	30	62	4.4	10.2	8.4
0	0	100	0	86	10	2.3	6.5	0
0	0	50	50[a]	43	55	1.2	3.3	6.9

[a] D-glucose.

[b] 2-Furaldehyde (on a mole basis, this is equivalent to 50% glucose).

[c] Press conditions 210°C, 10 min.

NH_4SSL improved its thermosetting properties, a result which could also be obtained through the addition of 2-furaldehyde.

The strength of the adhesive as measured by the TS test varies with the percentage of added sugar as shown in Figure 3. At a low press temperature of 210°C, crude NH_4SSL containing 20% reducing sugar gave poor adhesion, while pure D-glucose was totally ineffective; best results were obtained using 40–45% D-glucose in crude NH_4SSL. In contrast, higher temperatures resulted in an increased activity for crude NH_4SSL, while D-glucose alone also gave excellent results even in the absence of any NH_4SSL or any other acidic catalyst. Figure 4 shows the effect of adding catalytic amounts of ammonium sulfate to the NH_4SSL–glucose mixtures. As expected, the activity of pure glucose is increased by the addition of ammonium sulfate even at low press temperature.

Structural Features of Other Additives and Their Influence on Adhesive Properties

Having established that sugars or similar materials play an important role in the adhesion process, at the extreme, even in the absence of any NH_4SSL, our

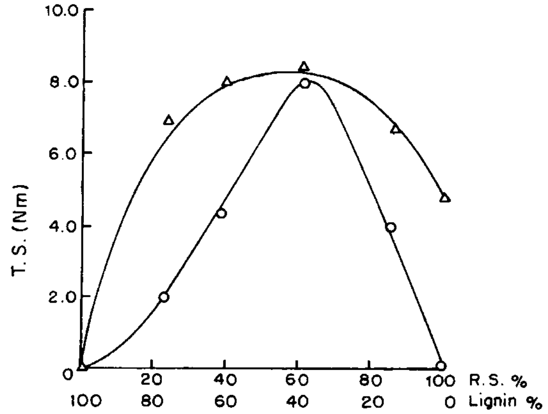


Fig. 3. Molded disc bonded with NH_4SSL–glucose adhesive: (△) 230°C; (○) 210°C.

The powders were ground to pass a Tyler sieve of 75-μm opening prior to mixing with wood particles.

Liquid formulations were used for some of the studies described in Tables I, II, and IV as several of the compounds tested as binders were either liquids or used with liquid additives. The compounds were dissolved in water or methanol at 40% concentration, and the desired amount of catalyst was added to the stirred solution. The % catalyst was calculated with respect to the weight of binder.

Acidification of CaSSL

Four portions of a single batch of CaSSL were acidified respectively with 2%, 4%, 6%, and 8% of concentrated sulfuric acid (% based on SSL solids), to convert the calcium lignosulfonate to lignosulfonic acid. After removal of the precipitated calcium sulfate by filtration, the filtrates, which contained mainly lignosulfonic acid, were dried to powders. The lignosulfonic acid content of the powder was determined by conductometric titration.[19]

Fractionation of NH_4SSL

The NH_4SSL was fractionated with an Amicon TC 5E thin channel ultrafiltration system fitted with a Diaflo DM5 membrane having a molecular weight cut off of 5000. In a typical experiment, 20 kg of NH_4SSL at 10% concentration was diafiltrated and washed with 60 kg of water through a DM5 membrane. The retentate (⅓ of total) having a nominal molecular weight over 5000, and the permeate (⅔ of total) having a nominal molecular weight below 5000, were concentrated separately to 50% solids, then transformed into powders by spray or vacuum drying. In other experiments, fractionations were made using a PM30 membrane with nominal molecular weight cutoff of 30,000.

Blending of Wood Particles and Binder

Both powdered and liquid binders were used with wood particles in 1:9 ratio (dry weights). The poplar wood particles which were used had average dimensions of 11.0 × 1.0 × 0.3 mm and were obtained by hammermilling veneers, followed by drying to 0% moisture. In the case of powdered materials, the binder was mixed with the dry wood in a rotary blender; liquid binder formulations were sprayed on the wood particles during blending, followed by removal of the solvent, if any, with a stream of air heated to 80°C.

Pressing and Testing of Molded Discs

Binder coated wood particles (22.7 g) were introduced into a cylindrical mold (56 mm diameter) preheated to 210–240°C as desired, and the press was then closed to stop (11 mm) for 10 min using a hydraulic pressure of 68.9 MPa. Only one disc size (56 × 11 mm) and one disc density (0.80 g/cm^3) were used in this study. The degree of curing of the resin binder was measured through a torsion-shear (TS) test,[20] which afforded a measure of the internal bond of the molded discs. A 25 × 25 × 11 mm specimen cut from the center of the disc was immersed in boiling water for 30 min; the specimen was then cooled for an additional 30 min in water at 20°C, and its mechanical strength measured with a standard torque wrench equipped with 25-mm sockets. For each binder formulation, three discs were made and tested; the data given in this report is the average of three TS measurements on the three samples.

Thermal Polymerization of Glyceraldehyde

A 5.0 g sample of DL-glyceraldehyde was placed between two 60 × 60 cm Teflon sheets. The Teflon sheets were themselves placed between two sheets of plywood (60 × 60 × 0.6 cm) and pressed at 240°C and 20.7 MPa for 10 min. The condensation product which was recovered weighed 2.6 g; it was studied by elemental analysis, acid hydrolysis, determination of the reducing sugar content, and IR spectroscopy. Essentially the same treatment was applied to samples of D-glucose and 5-(hydroxymethyl)-2-furaldehyde, although samples of the latter were pressed for 20 and 120 min.

Treatment of 2-Furaldehyde with Heat and Pressure

A 20 g sample of 2-furaldehyde was placed in a pressure vessel and pressurized to 24.1 MPa with compressed nitrogen and the vessel was heated to 175°C for 16 h. After treatment, the sample was still soluble in acetone and was used to make wood particle discs.

RESULTS AND DISCUSSION

Use of the Torsion Shear Test for the Comparative Evaluation of Wood Adhesive

A common way to investigate the rate of curing of a thermosetting resin is to subject it to different thermal treatments while measuring its change in molecular weight or its rate of insolubilization.[16,21] Unfortunately, the methods which can be used to measure the molecular weight of lignosulfonate by viscosity, osmometry, or gel permeation chromatography[22–24] are of limited value as the lignosulfonic acid insolubilizes under mild heat treatment. Measurements of the rate of insolubilization are also not fully satisfactory as the insolubilization is caused both by a polymerization and a loss of sulfonic acid groups. Another simple method to investigate the relative rate of curing of thermosetting resins is to compress the resins in a mold and heat them until they reach the crosslinked, insoluble, and infusible stage. The time required, at a given temperature, to reach this crosslinked stage is directly related to the reactivity of the material being studied. Since the bonding properties of a material are related to its ability to crosslink, an indirect measure of the extent of crosslinking can be obtained from the measurement of adhesive strength in the mechanical torsion shear (TS) test.[20] The main advantage of this test is that it is reproducible, requiring only a small sample of the material used as a binder, and that it can be correlated easily to the standard: Internal Bond Test CAN-3-0188.1-M78.[25] In a typical TS test, wood particles are coated with a few percent of the substance being investigated as a binder, and a solid disc is molded under heat and pressure to set the binder. The disc is then immersed in boiling water, and the wet torsion shear strength

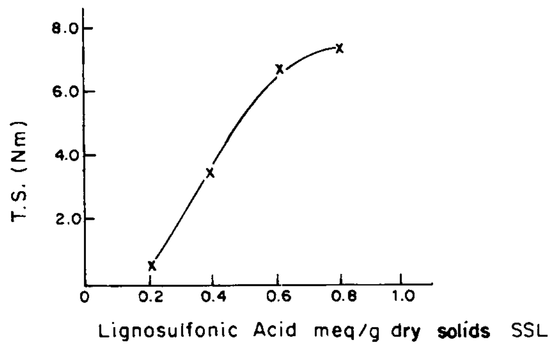


Fig. 1. Effect of lignosulfonic acid content on TS.

of the disc is measured. The validity of this simple test was verified in its application to the study of the adhesive strength of both acidified SSL and NH_4SSL as binders for molded discs under different conditions. The results shown in Figures 1 and 2 confirm that increased adhesive strength results from increasing the sulfonic acid content of the spent sulfite liquor, or from increasing the press temperature, in agreement with previous data.[19]

It is interesting to note (Fig. 2) that, while at low press temperature (190°C) the acidified SSL produces a disc with significantly higher TS strength than that obtained from NH_4SSL, this advantage is lost at higher press temperatures.

Reactive Species in NH_4SSL and Preliminary Study of Additives

A study of the adhesive properties of crude and fractionated NH_4SSL (Table I) indicates clearly that the carbohydrate components of the SSL make an essential contribution to its polymerization. While the high molecular weight fraction was unable to thermoset even under severe heat treatment, the lower molecular weight fraction, containing a large amount of reducing sugars, was much more reactive and possessed good binding properties. The active role of the carbohydrates in this polymerization process was clearly confirmed by an additional experiment in which equal amounts of the high molecular weight sugar-free SSL fraction and D-glucose was used. The mixture proved to have good binding properties, comparable to those of the low molecular weight (sugar-rich) SSL fraction. Similarly, the addition of D-glucose to the crude

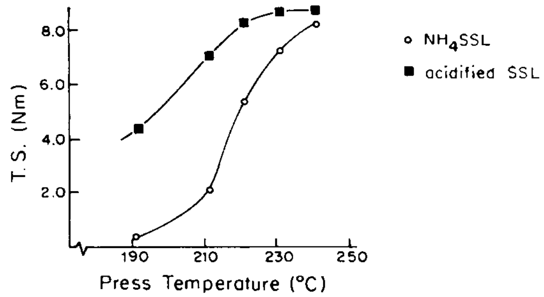


Fig. 2. Effect of press temperature on TS for NH_4SSL (○) and acidified SSL (■).

TABLE I
Effect of Fractionation and Additives on Bonding Properties of NH_4SSL

Crude NH_4SSL (wt %)	Ultrafiltrated MW 0–5000 (wt %)	Ultrafiltrated MW 5000 and up (wt %)	Additive (wt %)	Lignin (wt %)	Reducing sugars (wt %)	N (%)	S (%)	TS (Nm)[c]
100	0	0	0	68	22	2.8	6.5	2.0
50	0	0	50[a]	34	61	1.4	3.3	7.1
73	0	0	27[b]	50	—	2.0	4.7	6.6
0	100	0	0	30	62	4.4	10.2	8.4
0	0	100	0	86	10	2.3	6.5	0
0	0	50	50[a]	43	55	1.2	3.3	6.9

[a] D-glucose.

[b] 2-Furaldehyde (on a mole basis, this is equivalent to 50% glucose).

[c] Press conditions 210°C, 10 min.

NH_4SSL improved its thermosetting properties, a result which could also be obtained through the addition of 2-furaldehyde.

The strength of the adhesive as measured by the TS test varies with the percentage of added sugar as shown in Figure 3. At a low press temperature of 210°C, crude NH_4SSL containing 20% reducing sugar gave poor adhesion, while pure D-glucose was totally ineffective; best results were obtained using 40–45% D-glucose in crude NH_4SSL. In contrast, higher temperatures resulted in an increased activity for crude NH_4SSL, while D-glucose alone also gave excellent results even in the absence of any NH_4SSL or any other acidic catalyst. Figure 4 shows the effect of adding catalytic amounts of ammonium sulfate to the NH_4SSL–glucose mixtures. As expected, the activity of pure glucose is increased by the addition of ammonium sulfate even at low press temperature.

Structural Features of Other Additives and Their Influence on Adhesive Properties

Having established that sugars or similar materials play an important role in the adhesion process, at the extreme, even in the absence of any NH_4SSL, our

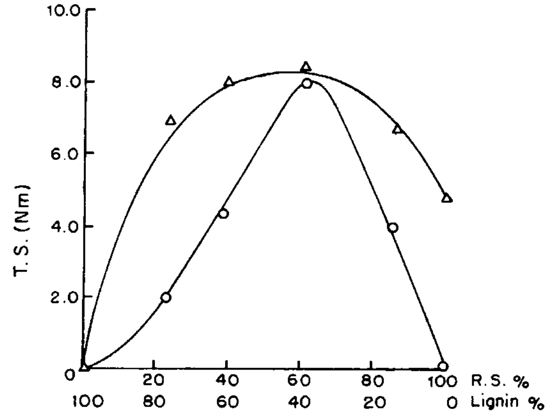


Fig. 3. Molded disc bonded with NH_4SSL–glucose adhesive: (△) 230°C; (○) 210°C.

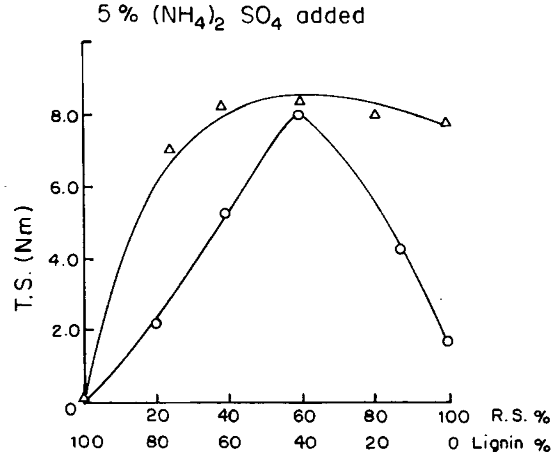
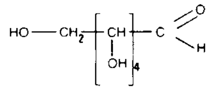
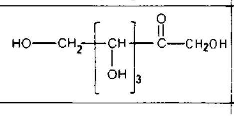
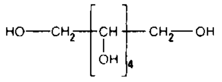
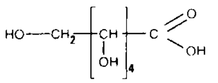
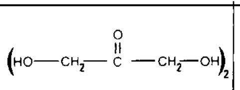
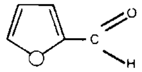
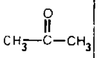
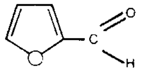
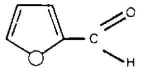
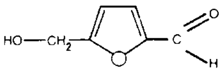
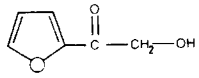
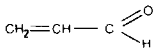
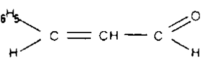


Fig. 4. Molded disc bonded with NH_4SSL–glucose adhesive containing 5% $(NH_4)_2SO_4$: (△) 230°C; (○) 210°C.

next objective was to establish which type of structural feature should be present in an additive to make it useful in the binding of wood particles. A number of different compounds were tested (Table II) in the preparation of wood particle molded discs without the addition of any NH_4SSL. As several of these additives have a low boiling temperature which causes some evaporation prior to reaching the desired press temperature, a catalytic amount of sulfuric acid was added in some experiments to increase the rate of curing and thus decrease evaporative losses. As it is likely that at least some evaporation had occurred in several instances, the values reported in Table II for the TS tests are probably lower than they would have been had a completely sealed system been available. Table II indicates that the presence of unsaturated aldehyde or keto-alcohol functionalities might be required for sugarlike additives to show good bonding properties. For example, no binding was observed with either a polyol such as glucitol or a hydroxy acid such as gluconic acid, while both glucose and fructose gave good results. These results also suggest that the reactive group is not only alkenic in nature as any dehydration which might be responsible for the polymerization of glucose would also likely occur with glucitol or gluconic acid. The lack of reactivity of the dimer of 1,3-dihydroxy-2-propanone is perhaps due to its inability to form a conjugated carbonyl compound by dehydration.

Surprisingly, both 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde are far less reactive than glucose. This observation is particularly puzzling in view of the large body of literature which suggests that furaldehyde derivatives are the active species which are involved in the carbohydrate polymerization process.[26–30] In the absence of acid catalyst and under conditions which afford best results with glucose, 2-furaldehyde failed to bind the wood particles. Weak binding was observed when 2% sulfuric acid was added and the disc was subjected to a higher pressure to produce a final disc density of 0.96 g/cm^3 instead of the usual value of 0.80 g/cm^3. Best results with 2-furaldehyde were obtained when the mixture of 2% acidic furaldehyde and wood particles was heated in a closed container at 80°C for 2 h prior to pressing into a disc. Under these conditions excellent adhesion was obtained and the product exhibited a TS test value of

TABLE II
Evaluation of Adhesive Properties of Selected Sugars and Related Polyfunctional Molecules

COMPOUND	FORMULA	BOILING POINT (50) AT 750 mmHg C	SOLVENT	H_2SO_4 % DRY RESIN	230°C-10 MIN T.S., Nm
D-GLUCOSE		...	H_2O	0	8.6
D-FRUCTOSE	 $HO-CH_2-[CH(OH)]_3-C(=O)-CH_2OH$	...	H_2O	0	8.0
GLUCITOL	 $HO-CH_2-[CH(OH)]_4-CH_2-OH$	400	H_2O	1	0
GLUCONIC ACID		...	H_2O	1	0
1,3-DIHYDROXY-2-PROPANONE DIMER	 $(HO-CH_2-C(=O)-CH_2-OH)_2$	...	H_2O	1	0
2-FURALDEHYDE [a]		161	 $CH_3-C(=O)-CH_3$	0	0
2-FURALDEHYDE [b]		161	CH_3OH	2	2.6
2-FURALDEHYDE [c]		161	CH_3OH	2	5.1
5-(HYDROXYMETHYL)-2-FURALDEHYDE		330	H_2O	0	1.7
2 FURYL HYDROXYMETHYL KETONE		...	CH_3OH	1	0
ACROLEIN CONTAINING 0.1% HYDROQUINONE		52	CH_3OH	1	3.5
CINNAMALDEHYDE		250	CH_3OH	1	2.5

a) Sample pre-heated in pressure reactor under 13.3 MPa(N_2) 16h

b) Disc compressed to a higher density of 0.96g/cm³ instead of 0.80g/cm³ used elsewhere in this study

c) Wood sample macerated in acidic-furaldehyde (2h, 80°C) prior to disc molding at 0.96g/cm³

5.1 Nm, a value similar to that obtained when furaldehyde is used in combination with NH_4SSL (Table I). This result suggests that perhaps some of the lignin which is contained in the wood chips was hydrolyzed by the acid and partially extracted by the 2-furaldehyde in the period which preceded pressing of the disc.

Positive results were also obtained with other unsaturated aldehydes such as acrolein or cinnamaldehyde. These results indicate that alternate mechanisms

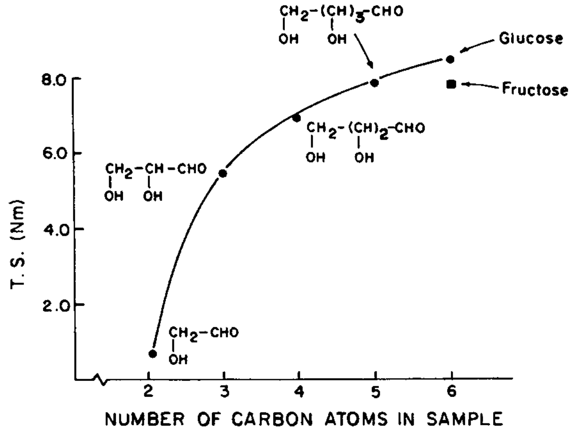


Fig. 5. Influence of carbohydrate chain length on TS.

not involving the formation of cyclic 2-furaldehyde derivatives might be operative in the polymerization of the carbohydrates of SSL.

To gain further insight in the possible mechanism of carbohydrate polymerization, a number of other sugars were also studied, including a homologous series with increasing chain length from a triose (glyceraldehyde) to a hexose (glucose). The relationship between carbon content and bonding efficiency under acid-free conditions is shown in Figure 5. Clearly satisfactory results were obtained in all cases; in fact, some bonding was even observed using the lower two-carbon homolog, glycolaldehyde. In contrast to the study of Heynes and Klier,[31] who reported that the thermal decomposition of glyceraldehyde proceeds via a route different from that of higher sugars, our limited experimental evidence suggests that, under a combination of heat and pressure, similar polymers are obtained from glyceraldehyde and glucose. Our evidence was obtained by polymerizing the sugars between two sheets of Teflon under conditions similar to those used in the preparation of molded discs. The infrared spectra of the solid materials which are obtained by polymerizing glyceraldehyde or glucose for 10 min at 200°C and 13.8 MPa are very similar (Fig. 6), while the infrared spectrum of the product obtained when 5-hydroxy-2-furaldehyde is subjected to a similar treatment is very different (Fig. 7) and does not show the strong band at 1730 cm^{-1}, which is found in the polymers of glyceraldehyde or glucose. It should also be noted

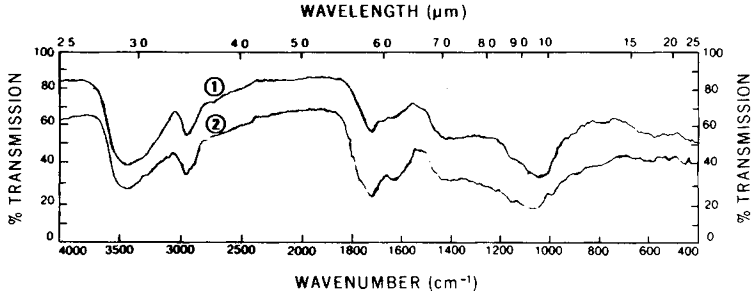


Fig. 6. Infrared spectra of D-glucose (1) and DL-glyceraldehyde (2) treated at 230°C and 13.8 MPa for 10 min.

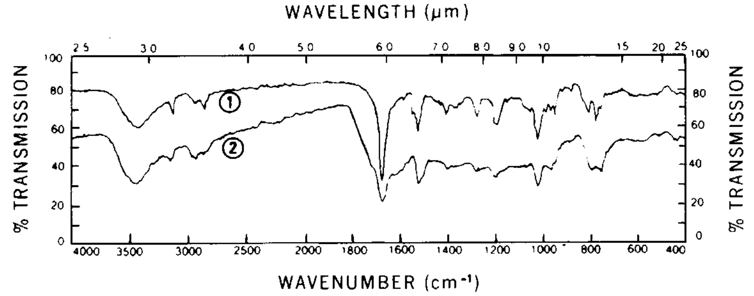


Fig. 7. Infrared spectra of 5-hydroxymethyl-2-furaldehyde after 30 min (1) or 120 min (2) treatment at 230°C and 13.8 MPa.

that the polymerization of the furaldehyde derivative was much slower, with no insolubilization or change in IR spectrum after a 30-min treatment. Insolubilization was eventually achieved after 120 min, but the IR spectrum of the final product still exhibited a prominent aldehydic absorption at 1680 cm^{-1}. An elemental analysis on the glyceraldehyde polymer showed that the polymerization had been accompanied by the loss of an average of 1.5 mol water/mol glyceraldehyde (Table III). In addition, the final product was found to be resistant to hydrolysis by aqueous acid.

Acid-Catalyzed Polymerization of Glucose and NH_4SSL

As was shown above, the thermal polymerization of NH_4SSL requires the presence of sugars and involves active species originating likely from both the lignosulfonate and the carbohydrate species. Since the addition of acid is known to catalyze the polymerization,[26–28] we studied the influence of the nature of the acid on the polymerization of glucose in an effort to determine which feature of the lignosulfonate might be responsible for its activity. The results of this study, shown in Table IV, seem to point to a clear correlation between acid strength and catalytic activity. It has recently been suggested by Laamanen[32] that the formation of a sulfonamide was a key step in the polymerization of NH_4SSL. As our study shows no catalytic activity for *p*-toluene sulfonamide, it is unlikely that sulfonamide species play a major role in the polymerization of the carbohydrates of SSL.

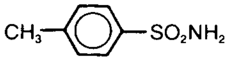
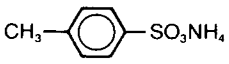
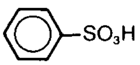
It is interesting to compare the results obtained in the polymerization of crude NH_4SSL (TS = 2.1 at 210°C) with those obtained in the polymerization of D-glucose in the presence of ammonium sulfate or *p*-toluenesulfonate (TS = 2.1

TABLE III
Elemental Analysis of DL-Glyceraldehyde before and after Thermal Treatment

Sample	Elemental analysis C (%)	H (%)	O (%)	Reducing sugar (%)
DL-glyceraldehyde	40.6	6.7	52.7	100
DL-glyceraldehyde[a] after thermal treatment	59.1	5.1	35.8	0[b]
(Calculated) DL-glyceraldehyde, less 1.5 mol H_2O	57.1	4.8	38.1	—

[a] Press conditions 240°C, 10 min, 20.7 MPa.
[b] After boiling in dilute H_2SO_4.

TABLE IV
Effect of Different Catalysts on Adhesive Properties of D-Glucose

CATALYST	CATALYST % DRY D-GLUCOSE AT 40% H_2O SOLUTION	PRESS TEMPERATURE °C	T.S., Nm
NIL	0	230	5.1
NIL*	0	230	0
HEXAMETHYLENETETRAMINE	5	220	0
$(NH_4)_2CO_3$	5	220	0
	5	220	0
	5	210	2.1
$H_2NCH_2CH_2COOH$	5	220	0
NH_4HSO_4	5	210	2.8
	2	210	8.5
H_2SO_4	2	210	8.6

* 10% Moisture content, all others were anhydrous.

at 210°C). Although the similarity in TS values is likely to be a coincidence, it could suggest that the active site of NH_4SSL is the sulfonate group, not a free lignosulfonic acid group which would have been expected to give a much higher TS value with crude NH_4SSL. In fact, we failed to detect any free lignosulfonic acid in a study of the pyrolysis of NH_4SSL, and observed that the pyrolysis was accompanied by a loss of both sulfur and nitrogen in 1:1 molar ratio. A similar observation was also made in the pyrolysis of a 1:1 mixture of NH_4SSL and glucose.

CONCLUSION

Although no definite answers can be provided on the polymerization mechanism and the respective roles of NH_4SSL and carbohydrate species in the binding of wood particles, this study shows clearly that both lignosulfonate and sugars contribute to the polymerization of SSL. The dehydration of carbohydrates is catalyzed by ammonium lignosulfonate or lignosulfonic acid, which are both acid catalysts. Under a combination of heat and pressure, the sugars may homopolymerize or copolymerize with lignosulfonate and/or desulfonated lignin via participation of both carbonyl and carbon–carbon double bond functionalities.

References

1. K. V. Sarkanen and C. H. Ludwig, "Definitions and Nomenclature," in *Lignins*, K. V. Sarkanen and C. H. Ludwig, Eds., Wiley, New York, 1971, p. 1.
2. K. C. Shen, U.S. Pat. 4,193,814 (1980).
3. K. C. Shen, D. P. C. Fung, and L. Calvé, U.S. Pat. 4,265,846 (1981).
4. S. A. Rydholm, *Pulping Processes*, Wiley Interscience, New York, 1965, p. 284.
5. E. Adler, "Lignin Chemistry, Past, Present and Future," *Wood Sci. Technol.*, **11**, 169–218 (1977).
6. D. W. Glennie, "Reactions in Sulfite Pulping," in *Lignins*, K. V. Sarkanen and C. H. Ludwig, Eds., Wiley, New York, 1971, pp. 597–631.
7. G. Gellerstedt, *Sven. Papperstidn.*, **79**, 537 (1976).
8. L. Ivnäs and B. Lindberg, *Acta Chem. Scand.*, **15**, 1081 (1961).
9. J. Gierer and S. Söderberg, *Sven. Papperstidn.*, **63**, 201 (1960).
10. Y. Z. Lai and K. V. Sarkanen, "Isolation and Structural Studies," in *Lignins*, K. V. Sarkanen and C. H. Ludwig, Eds., Wiley, New York, 1971, p. 182.
11. K. Freudenberg, G. Maerker, and H. Nimz, *Chem. Ber.*, **97**, 903 (1964).
12. D. Glennie, *Tappi*, **49**, 237 (1966).
13. E. Adler, *Sven. Papperstidn.*, **54**, 477 (1951).
14. V. M. Nikitin, *Khim. Drev.*, **7**, 37 (1971).
15. A. Alekseev, K. Forss, M. Johanson, and B. Stenlund, *Pap. Puu—Papper och Trä*, **60**(4a), 195 (1978).
16. F. W. Herrick, R. J. Engen, and O. Goldschmid, *Tappi*, **62**, 81 (1979).
17. K. C. Shen and L. Calvé, *Adhes. Age*, **23**, 25 (1980).
18. D. P. C. Fung, K. C. Shen, and L. Calvé, Eastern Forest Products Laboratory Information Report #OPX180E, Canadian Forestry Service, Ottawa, Ont., 1977.
19. D. P. C. Fung, K. C. Shen, and L. Calvé, Tappi Conference Proceedings, Forest Biology Wood Chemistry Conference, Madison, Wisc., 1977, p. 257.
20. K. C. Shen and M. N. Carroll, *For. Prod. J.*, **19**, 17 (1969).
21. Y. Kyogoku and Y. Hachihama, *Osaka Univ., Technol. Rep.*, **5**, 199 (1955).
22. E. Nokihara, M. J. Tuttle, V. F. Felicetta, and J. L. McCarthy, *J. Am. Chem. Soc.*, **79**, 4495 (1957).
23. H. H. Brownell, *Tappi*, **53**, 1278 (1970).
24. K. G. Forss, B. G. Stenlund, and P. E. Sagfors, *J. Polym. Sci., Appl. Polym. Symp.*, **29**, 1185 (1976).
25. "Interior Mat-Formed Wood Particleboard," Canadian Standards Association, CAN3-0188.1-M78, National Standards of Canada, Rexdale, Ont., 1978, p. 13.
26. E. F. Anet, *Adv. Carbohyd. Chem.*, **19**, 181 (1964).
27. M. S. Feather and J. F. Harris, *Carbohyd. Res.*, **15**, 304 (1970).
28. K. Heynes and R. Auber, *Liebigs Ann. Chem.*, **733**, 159 (1970).
29. F. Shafizadeh and Y. Z. Lai, *Carbohyd. Res.*, **40**, 263 (1975).
30. V. Prey, W. Eichburger and H. Gruber, *Stärke*, **29**, 60 (1977).
31. K. Heynes and M. Klier, *Carbohyd. Res.*, **6**, 436 (1968).
32. L. Laamanen, *J. Polym. Sci., Appl. Polym. Symp.*, **28**, 1139 (1976).

Received October 6, 1982
Accepted January 10, 1983