Influence of Resin Formulation Variables On Bond Quality of Southern Pine Plywood

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Abstract

Thirty-six resins, each with two replicates, were factorially prepared with three formulation variables: molar ratios of sodium hydroxide to phenol of 0.4, 0.7, and 1.0; levels of resin solids content of 37, 40, and 43 percent; and molar ratios of formaldehyde to phenol of 1.6, 1.9, 2.2, and 2.5. Glue bond quality decreased substantially with a change of NaOH/phenol ratio from 0.4 to 0.7. A further change in ratio from 0.7 to 1.0 failed to affect it significantly, apparently because conversion of formaldehyde by the Cannizzaro reaction became important where more than half a mole of caustic was present in the reaction mixture. On the average, bond quality increased as solids content increased. Changes in the CH_2O/phenol ratio affected delamination but not wet shear strength or wood-failure percentages; the lower molar ratios yielded gluelines that delaminated least. Latewood-to-latewood delaminated substantially more than earlywood-to-earlywood gluelines. Of 72 batches of resins, two met the wood-failure standard for exterior gluelines. Three yielded latewood-to-latewood gluelines that averaged less than 20 percent delamination in 3 months of outdoor exposure in central Louisiana.

PREVIOUS PAPERS have examined the relationships between basic properties of phenolic resins and glueline performance in southern pine plywood. Surface tension, contact angle, curing properties, and alkalinity of the resins were shown to be related to bond quality (Hse 1971, 1972a, b). The analyses were chiefly in terms of single resin properties. Any change in formulation variables, however, is likely to have interrelated effects on these properties. In the present research, therefore, changes in formulation variables were evaluated directly in terms of bond quality. No attempt was made to develop an optimum resin. Rather, the purpose was to explore a range of formulations in order to define effects of three main variables. Special attention was paid to sodium hydroxide content, since determination of the optimum catalyst ratio would be very useful in developing phenolic resins for commercial use.

Procedure

Resin Preparation

All phenol formaldehyde resins were prepared in the laboratory; formulation variables were as follows:

1) Molar ratio of sodium hydroxide to phenol (NaOH/phenol)—0.4, 0.7, and 1.0.
2) Molar ratio of formaldehyde to phenol (CH_2O/phenol)—1.6, 1.9, 2.2, and 2.5.
3) Concentration of reaction mixture (percent of solids by weight)—37, 40, and 43.

Thus, 36 resins were formulated; as each was replicated, 72 batches of resins were prepared.

To prepare each resin, all of the phenol, formaldehyde, and water was placed in the reaction kettle. The sodium hydroxide was added, as a catalyst, in three steps; *i.e.,* 0.3 mole of sodium hydroxide per mole of phenol was added at the beginning, and the balance was divided into two equal parts, one of which was added 30 minutes after the reaction began and the other a half-hour later. To initiate the reaction, the mixture was quickly heated and maintained at 96-100°C. (reflux temperature). When viscosity reached 3.2 stokes (ASTM Method D 1545-63) the temperature was reduced to 80°C. When viscosity reached 9.0 stokes the reaction was terminated by rapidly cooling the mixture to 25°C.

Evaluation of Glue Bond Quality

Glue bond quality was evaluated by wet shear strength and percent of wood failure in specimens subjected to the vacuum-pressure cycle for exterior glue lines (PS-1-66), and by delamination (expressed as percent of glueline area) after 3 months of exterior exposure.

Veneers were of southern pine, 1/8-inch thick. One 12- by 12-inch three-ply panel was glued up for each of the 72 batches of resins, and 20 standard shear

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Table 1. — SHEAR STRENGTH, WOOD FAILURE, AND DELAMINATION RELATED TO RESIN FORMULATION VARIABLES.[1]

Percent solids content	Molar[1] ratio F/P	Shear strength[2]	Wood failure[2]	Delamination E/E[1,2]	Delamination L/L[1,2]	Delamination Avg.[3]
		Psi				
0.4 mole NaOH/mole phenol						
37	1.6	266	76	0.1	78.4	39.3
37	1.9	290	75	0.7	27.4	14.1
37	2.2	259	79	0.3	67.7	34.0
37	2.5	286	71	5.0	87.0	46.0
40	1.6	306	60	0.1	57.2	28.7
40	1.9	290	82	1.0	54.0	27.5
40	2.2	279	75	0.1	34.2	17.2
40	2.5	267	78	1.0	55.0	28.0
43	1.6	303	69	0.6	20.8	10.7
43	1.9	289	75	0.0	29.9	15.0
43	2.2	268	76	0.2	83.0	41.6
43	2.5	273	64	0.8	88.5	44.7
0.7 mole NaOH/mole phenol						
37	1.6	154	30	10.3	16.9	13.6
37	1.9	159	38	16.9	97.5	57.2
37	2.2	150	30	7.0	99.5	53.3
37	2.5	176	27	1.6	97.4	49.5
40	1.6	245	50	1.4	96.2	48.8
40	1.9	248	66	20.8	86.7	53.8
40	2.2	197	51	15.6	89.0	52.3
40	2.5	213	48	0.9	95.8	48.4
43	1.6	246	61	3.4	66.9	35.2
43	1.9	258	63	0.0	47.4	23.7
43	2.2	264	66	2.3	85.3	43.8
43	2.5	238	54	0.1	97.0	48.6
1.0 mole NaOH/mole phenol						
37	1.6	255	50	17.2	98.4	57.8
37	1.9	168	25	2.4	98.2	50.3
37	2.2	157	28	4.9	72.5	38.7
37	2.5	160	21	27.7	100.0	63.9
40	1.6	216	50	6.6	99.0	52.8
40	1.9	223	65	6.0	100.0	53.0
40	2.2	220	58	10.6	96.9	53.8
40	2.5	252	55	45.4	87.4	66.4
43	1.6	244	62	0.4	83.6	42.0
43	1.9	233	45	2.9	72.3	37.6
43	2.2	262	58	8.2	88.4	48.3
43	2.5	246	57	0.1	76.3	38.2

[1]F means formaldehyde; P means phenol; E/E means earlywood-to-earlywood, L/L means latewood-to-latewood bonds.

[2]Values are averages of 40 samples.

[3]Values are averages of 80 samples.

specimens were cut from each panel in such a manner that half could be pulled open and half closed. For exposure specimens, five two-ply cross-laminated panels were glued up for each resin and sawn into 0.5-inch squares to yield 20 earlywood-to-earlywood (E/E) exposure specimens and 20 latewood-to-latewood (L/L) specimens.

Details of sample preparation and testing have been described previouslv (Hse 1968, 1971).

General gluing conditions were:

Glue mix: 26 percent resin solids in the mixed glue
Spread: 75 pounds per 1,000 square feet of double glueline
Closed assembly time: 20 minutes
Hot press temperature: 285°F.
Hot press time: 6-1/2 minutes
Specific pressure: 175 psi

Results and Discussion

Table 1 summarizes average wet shear strength, percentage of wood failure, and percentage of delamination for each combination of resin formulation variables. By all three methods of evaluation, bond quality differed significantly (0.05 level) with change in NaOH/phenol ratio and resin solids content. The change in CH_2O/phenol ratio was significant only in the delamination test.

As shown in Table 2, a change in NaOH/phenol ratio from 0.4 to 0.7 substantially decreased bond qualities. Shear strength dropped from 281 to 212 psi, wood failure declined from 73 to 49 percent, and delamination changed from 54 to 81 percent for L/L gluelines. With an increase in NaOH/phenol ratio from 0.7 to 1.0, changes in bond quality were not significant by Duncan's (1955) analysis. This result suggests that there may be a critical concentration of sodium hydroxide beyond which no significant improvements can be obtained.

To examine this assumption, an attempt was made to study resin polymerization under the reaction conditions of the study. It is generally accepted that the polymerization involves three reactions (Fig. 1): addition of formaldehyde to the phenolic molecule to form methylol groups (reaction 1) and a condensation reaction between methylol groups of one molecule and the ring hydrogen (reaction 2) or methylol groups of another phenolic molecule (reaction 3) with the formation of methylene linkage.

As the reactions proceed, the formaldehyde concentration and methylol content of the mixture change

Table 2. — EFFECT OF RESIN FORMULATION VARIABLES ON SHEAR STRENGTH, WOOD FAILURE, AND DELAMINATION.

Variables	Shear strength	Wood failure	Delamination[1] E/E	Delamination[1] L/L	Delamination[1] Average
	Psi	Percent			
Molar ratio of NaOH to phenol					
0.4	281	73	1	54	28
0.7	212	49	9	81	45
1.0	219	48	11	89	50
Concentration of reaction mixture (percent of solids by weight)					
37	206	46	10	76	43
40	246	61	9	79	44
43	260	62	2	70	36

[1]E/E means earlywood-to-earlywood, L/L means latewood-to-latewood bonds.

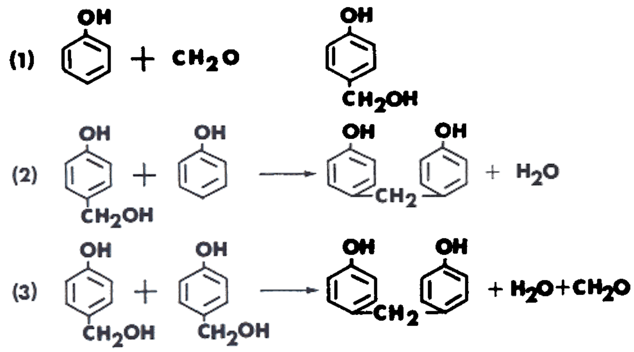


Figure 1 Summary of chemical reactions between phenol and formaldehyde under alkaline condition.

according to the reaction rates. Viscosity of the mixture rises with increases in the length of the molecular chain resulting from the condensation reaction. For these reasons, formaldehyde concentration, methylol content, and viscosity were expressed as a function of reaction time. Formaldehyde concentration was expressed by a method involving titration with hydroxylamine-hydrochloride (Walker 1964, pp. 493-494), viscosity was measured by Brookfield viscometer, and methylol content was estimated by a method previously described (Hse 1972a).

The sodium hydroxide catalyst caused a very rapid addition of methylol groups; after 30 minutes of the reaction, the methylol content (as measured by absorbance ratio—see Fig. 2A) attained its highest level, and more than 95 percent of the formaldehyde was consumed. Significant differences in the formaldehyde concentration were detected at the end of the second sodium hydroxide addition (*i.e.*, at 60 minutes' reaction time): the concentration increased at an NaOH/phenol ratio of 0.4 and decreased at NaOH/phenol ratios of 0.7 and 1.0. This difference seemed important and was studied further.

The increase in formaldehyde concentration may signify condensation reactions between two methylol groups of two phenol alcohols; studies have shown that replacement of methylol groups occurs more rapidly than that of ring hydrogen under alkaline conditions (Ziegler and Zigeuner 1948; Freeman and Lewis 1954). The decrease in formaldehyde concentration at NaOH/phenol ratios of 0.7 and 1.0 may result from addition of methylol groups, but more probably is caused by conversion of formaldehyde to methanol and formic acid by the Cannizzaro reaction.

Because methylol content—measured as absorbance ratio 1010/1210—decreased at approximately the same rate for all NaOH/phenol ratios between 30 to 60 minutes of the reaction, the ratio of methylol group formation (by addition reaction) to consumption (by condensation reaction) likely remained the same. If the decreasing formaldehyde concentrations at NaOH/phenol ratios of 0.7 and 1.0 indicated a higher rate of addition of methylol groups, then consumption must also have been higher. Faster consumption, however, is not likely, for Granger (1937) has shown that an increase in amount of catalyst above approximately 0.05 mole percent of caustic has no effect on the rate of condensation. Furthermore, viscosity measurements (Fig. 2B) indicated that the higher caustic content retarded the condensation reaction. The decrease in formaldehyde concentration is, therefore, largely attributed to the Cannizzaro reaction, *i.e.*, the Cannizzaro reaction competed with the addition reaction for the formaldehyde. Figure 2B indicates that, at NaOH/phenol ratios of 0.7 and 1.0, the formaldehyde deficiency may have deterred addition of methylol groups sufficiently to prolong the condensation reaction. The prolonged reaction of the resin may result in declining chemical reactivity and, in turn, poor bonds. This explanation is

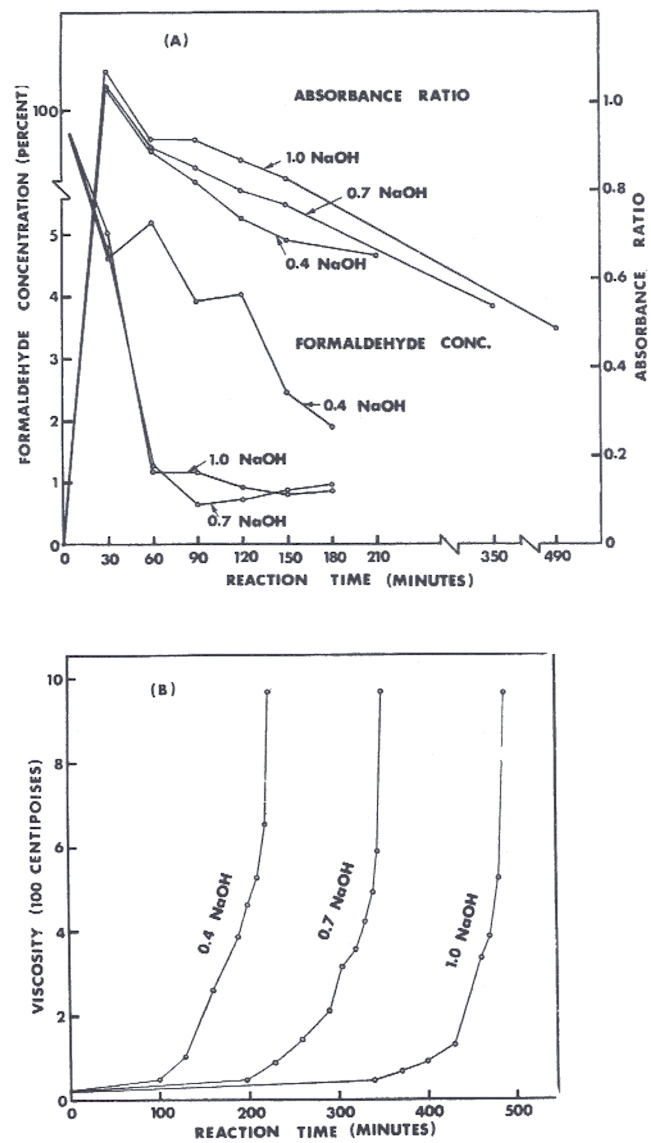


Figure 2. — Formaldehyde concentration and absorbance ratio (A) and viscosity (B) as related to reaction time. Absorbance ratio means infrared absorbance of methylol band at 1010 $cm.^{-1}$ divided by absorbance of the phenolic hydroxyl band at 1210 $cm.^{-1}$.

supported by the fact that the resin produced with higher NaOH/phenol ratio had lower methylol content (Fig. 1A) and longer cure time (Hse 1971).

An important aspect of the Cannizzaro reaction is its relationship to caustic level. After the second caustic addition, the close grouping of formaldehyde concentration for NaOH/phenol ratios of 0.7 and 1.0 seems to indicate that the Cannizzaro reaction becomes significant when more than half a mole of sodium hydroxide is present in the reaction mixture (*i.e.*, caustic content is 0.5 mole for NaOH/phenol ratio of 0.7 at the end of the second caustic addition). However, the critical concentration of caustic may be any point above 0.4 mole.

On the average, glue bonds were best with 43 percent resin solids and poorest with 37 percent resin solids (Table 2). It is generally recognized that resins formulated with lower solids content have higher molecular weights, if all other conditions are equal. The high-weight resins, with their fast cure, are usually desirable for southern pine plywood, but they create problems of glueline dry-out. The present data therefore indicate that the effect of dry-out on bond quality is more important than that of cure rate. Ripley (1967) has estimated that glueline dry-out causes approximately 85 percent of the poor bonds in southern pine plywood.

The effects of CH_2O/phenol ratio on delamination are plotted in Figure 3. The resins formulated with ratios of 1.6 and 1.9 yielded stronger glues than were obtained from ratios of 2.2 and 2.5. This result is in agreement with industrial experience. Booth (1958) reported that firms producing phenol-formaldehyde resins have in general favored a ratio of 2, since additional formaldehyde will not react effectively.

Although the resin with a ratio of 1.6 performed as well as that with a ratio of 1.9, it tended to yield a product having a longer cure time (Hse 1971).

Resin solids content interacted with NaOH/phenol ratio to affect bond quality. At a ratio of 0.4, the effect of sodium hydroxide predominated and bonds varied only slightly as solids content increased. But at

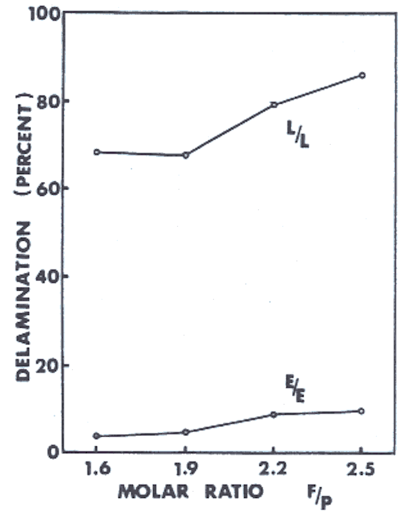


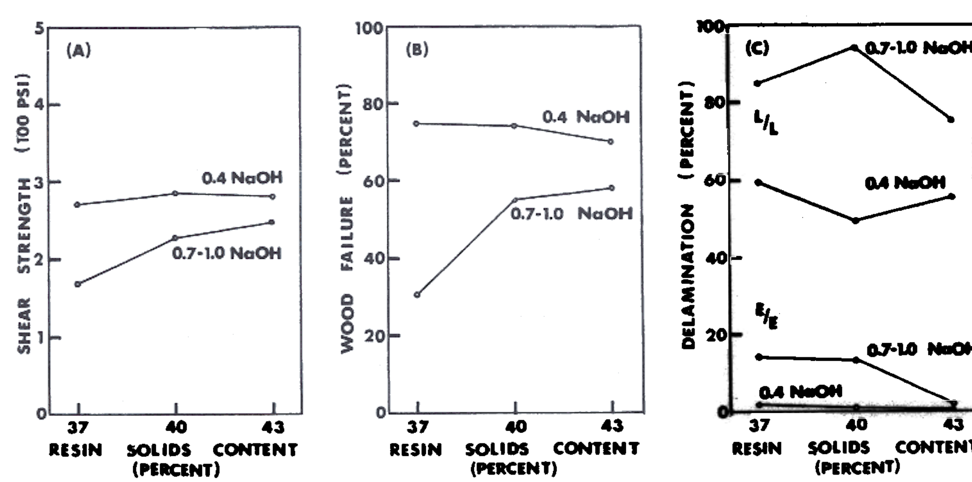
Figure 3. — Relationship between delamination and CH_2O/phenol ratio for latewood/latewood (L/L) and earlywood/earlywood (E/E) bonds.

ratios of 0.7 and 1.0 substantial gains in bonding accompanied increases in solids content, the sole exception being the latewood-to-latewood gluelines at 37 percent solids content. These results are graphed in Figure 4; since performance at ratio 0.7 did not differ from that at ratio 1.0, data for the two ratios are combined in the figure.

The L/L delamination was substantially higher than the E/E: 75 percent as compared to 7 percent (Table 1). Of the 36 resins, one with an L/L delamination of 17 percent was obtained. This was significantly better than the average of more than 80 percent obtained at 15 minutes' assembly time in a previous study (Hse 1968).

On the basis of wood failure, two batches of resins among the 72 met the standard of vacuum-pressure soak cycle for exterior glueline (PS-1-66). Shear strength and wood failure were positively correlated, as shown by regression analysis (Fig. 5). Delamination values, however, were correlated with neither shear strength nor

Figure 4. — Interactions of wet shear strength (A), wood failure (B), and delamination (C) with NaOH/phenol ratio and solids content.



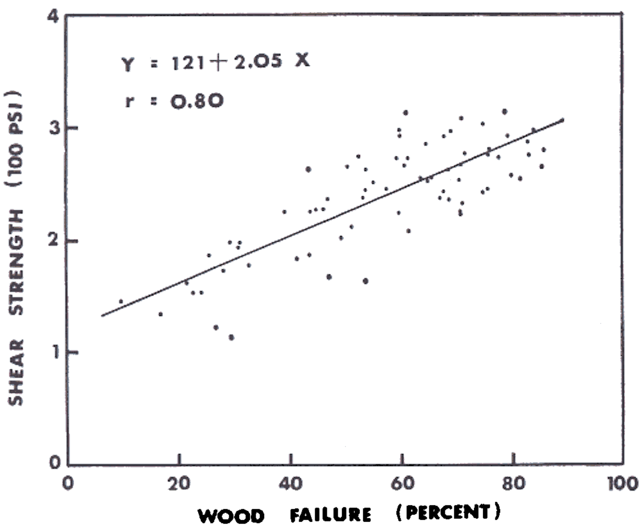


Figure 5. — Wood failure as related to wet shear strength.

wood failure. Probably extreme wood variation between L/L and E/E specimens obscured significant relationships.

Of the three formulation variables, the NaOH/phenol ratio gave the most surprising results. The ratio of 0.4 is considerably lower than any used in industry, but resins thus catalyzed gave consistently better bonds than those with higher proportions of caustic. This result seems to indicate the importance of controlling the Cannizzaro reaction in resin formulation. A study of various methods of adding sodium hydroxide is in progress and may provide a basis for optimizing the ratio.

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